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P. Ramsborg

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TRANSACTIONS.

RAMMELSBERG MEMORIAL LECTURE.

(Delivered on December 13th, 1900).

By H. A. Miers, M.A., D.Sc., F.R.S., Waynflete Professor of Mineralogy in the University of Oxford.

The Chemical Society has recently become only too familiar with the death of foreign members of patriarchal age, otherwise it would be difficult to realise that a chemist whose death took place last year was the friend and associate of Berzelius. The man whose life and work we commemorate to-day was an almost exact contemporary of another famous chemist whose great genius and high character have been recently depicted for us by his friend and fellow-worker. Rammelsberg was born two years later than Bunsen and outlived him by less than one year.

Among the workers who during this period contributed to raise the edifice of modern chemistry upon the foundations laid during the childhood of these two men, some, like Bunsen, were thinkers of the highest genius whose inspiring ideas directed the development of the structure, others, like Rammelsberg, were the skilful and indefatigable craftsmen who amassed and set in order the material. Owing to the fact that Rammelsberg's name is not associated with any of the great discoveries of a period which belongs mainly to organic chemistry, and that he purposely confined his life-work to inorganic research, there is some danger lest the value of his contributions to science should be underrated, except, indeed, among mineralogists; I am, therefore, particularly glad to have this opportunity of sketching a brief record, however imperfect, of his colossal labours. It will be made clear, I

hope, that, although brought up in the school of Berzelius, Rammelsberg was by no means one who ignored the progress of the modern chemistry, but did, in fact, contribute in no small degree to its dissemination. To those among the younger generation of organic chemists who know anything of his work, the name of Rammelsberg will, I imagine, evoke the recollection of a vast number of papers whose titles relate to mineral and other inorganic analyses and to crystallographic measurements; they may only know him as a patient worker and think of him as one who pursued his labours undisturbed by the growth of modern chemistry. This would be a very false estimate, and in order to dismiss such a misconception at the outset, I cannot do better than quote the words addressed to Rammelsberg on the occasion of his Doctor's Jubiläum, I believe by Hofmann, on behalf of the Berlin Academy of Sciences. After describing his labours in practical chemistry, he says, "It was not only the empirical but also the theoretical side of science which attracted your lively attention. Originally brought up in the school of Berzelius, and the contemporary of Heinrich and Gustav Rose, of Mitscherlich and Wöhler, you subsequently witnessed all the changes which chemical theory has experienced up to the present day. With a quick eye you recognised early the advantages of the present views and *you were among inorganic chemists the first to adopt the new system of formulæ.*"

While I am glad that it has fallen to my lot to recall these features of his life-work, I regret that I never had the opportunity of even seeing the man whom I have to describe. Whatever impression of his life and work I may succeed in conveying is derived solely from a study of his publications or from the reminiscences of others to whom he was personally known; and he was a man who more than any other led the uneventful laborious life of a student.

Among the day dreams to which most persons have yielded, is the fascinating speculation as to what would have been their lot had their life been set in earlier times. Could any chemist choose for himself a more attractive period than the early part of the nineteenth century, when the influence of Berzelius had entered into the heart of the science? In the youth of Rammelsberg, the electro-chemical theory had overcome all opposition and supplied a great principle of apparently universal application; the modern methods of analysis were being perfected; and the chemist was for the first time really equipped for conquest in the fields of research. It is a commonplace of historical criticism that in the early history of any art there is a period when the materials, the instruments, and the methods have just been matured, although the art has not become self-conscious; when the artist revels in his newly-acquired powers, and finds a pleasure in the exercise of the chisel or the brush without any thought of whither

his work tends or what purpose it is to serve. Something analogous happens, I think, in the early history of a science, and at the time when Rammelsberg began to work, a chemist must have felt that every analysis which he could make, every substance which he could prepare, was something new, of unknown import, and involved the exercise of new powers. To a young, ardent, and ambitious student, this in itself must have been an overpowering impulse to energetic labour; in no life is this delight in work better exemplified than in that of Rammelsberg.

Karl Friedrich Rammelsberg was born on April 1st, 1813, at Berlin. He was of humble origin, and was entirely a self-made man; his family came from Altenbrak an der Bode in the Harz; his father was in quite a small way of business in Berlin. As a boy he was educated in a private school, and in the Friedrich Werder Gymnasium; he then entered the Realschule, in the Kochstrasse, where he seems to have received some little scientific training from the director, Spillecke. Here he remained for four years, and leaving at the age of 15 entered the Koch Apotheke, where he studied for the next four years, with the view of becoming an apothecary. In this Apotheke he seems to have learnt botany from Hayne and pharmaceutical chemistry from Heinrich Rose; under the latter, Rammelsberg must have first become acquainted with the spirit of scientific research, and he himself says that he never forgot the teaching of this man, from whom he received such varied and valuable assistance. In 1832, at the age of 19, he obtained a place in the Apotheke at Dardesheim, near Halberstadt. After remaining there only one year, the young chemist took the step which determined his whole future career; he suddenly abandoned the line of life upon which he had entered, and returned to Berlin with the object of obtaining a university education and devoting himself to pure science; this step was probably taken by Rose's advice: it must have required great determination for a lad of his education and antecedents to enter this new world, and compete for the distinctions gained by men of the calibre of Mitscherlich and Heinrich Rose. In order to pass in the necessary examinations in Latin and Greek, he was obliged to teach himself unaided the latter language. This was accomplished at odd moments and in the intervals between other studies. In 1834, he was able to pass his Maturitätsexamen at the Gymnasium zum grauen Kloster, and was matriculated. Erman and Magnus were at this time the professors of physics, Mitscherlich and Heinrich Rose of chemistry, Weiss and Gustav Rose of mineralogy; with all these he worked, as well as with Hoffmann in geology. His Arbeit was carried out in Mitscherlich's laboratory and was a dissertation entitled "De cyanogenii connubiis nonnullis" (1837). The titles of his four doctoral theses are interesting in the light

of the researches to which he devoted the remainder of his life; they were entitled:

(1) Experientia chemica in constituendis theoriis geologicis praecipue est observanda.

(2) Connubia chemica organica et inorganica haud absolute discerni possunt.

(3) In systematibus, quæ hucusque exstiterunt, chemicis theoria deflagrationis summum tenet locum.

(4) Systema mineralogicum *naturale* neque indolem externam neque internam fossilium negligere debet.

A man's early work is generally a clue to his subsequent tendencies, and Rammelsberg's theses are no exception; his interest in inorganic chemistry and in substances like the cyanides, which lie on the borderland between the organic and inorganic; his leaning towards the geological aspects of chemistry; his life-long study of both the chemical composition and the crystalline form of minerals, are all foreshadowed in these titles.

Three years later he began to teach at the Hochschule; in 1841, he was "habilitated" as Privatdocent at the university, and was also a teacher at the Handels-Schule.

At the age of 24 (in 1837), he had already begun to publish analyses of inorganic compounds and minerals—the opening of a long series of researches in inorganic chemistry and mineralogy, many of them lengthy and laborious memoirs, which issued in an unbroken stream from 1838 to 1888.

When he became Privatdocent there were only two laboratories in Berlin where a student could work, namely, those of Heinrich Rose and Mitscherlich, and in these only a few specially recommended pupils could find a place; Rammelsberg, therefore, with characteristic energy, started a private laboratory of his own in which all his earlier pupils must have obtained their experience; it was so small that only two students could be accommodated at a time, and when one pair went off a second pair came on; the fee was the ridiculously small one of 50 pfennigs. With this scanty help, he was also able to assist his mother to support herself.

This small beginning was really the initiation of practical laboratory instruction in Berlin, and was the seed from which sprang the second chemical institute of which Rammelsberg was ultimately made the first director. His time must have been very fully occupied, and yet not only did the publication of scientific papers continue unabated, but he began to add to them the first of a series of text-books and of monumental works of reference: in 1841 his dictionary of chemical

mineralogy, in 1842 his text-book of stochiometry and theoretical chemistry. In a very short time he became a recognised authority on chemistry, mineralogy, crystallography, and metallurgy.

In 1846, he was appointed Professor extraordinarius of inorganic chemistry, and in 1850 he was also made instructor in chemistry at the Gewerbe-akademie, where he was at last provided with an adequate chemical laboratory; this academy ultimately developed into that splendid institution, the Technische Hochschule of Charlottenburg. He was also instructor at the Mining Academy from the time of its foundation in 1860. In 1855, he was made a member of the Berlin Academy.

It was not until 1874 that Rammelsberg attained the full recognition of his labours and was made ordinary Professor of inorganic chemistry (in succession to Heinrich Rose), a position to which he had raised himself from a lowly origin and by the exercise of the most extraordinary industry.

In 1846 he married the daughter of a man well known in the history of mineralogy, Oberbergrath Zincken, of Mägdesprung.

He took an active part in the foundation of the Berlin Chemical Society in 1868, and was its President in 1870 and 1874.

From the impression which I have derived from those who knew him, he must have been a man of unusually short stature, energetic carriage, and somewhat austere manner; an early photograph represents, by the sharply-cut features, the keen eye, and the compressed lips, a man of precision and determination; he was clear and concise as a lecturer; a very quick but accurate worker; sharp in exposing the mistakes of others, but equally ready to learn from them and correct his own errors.

Professor Liveing, who worked in his laboratory at the Gewerbe-akademie in 1852, kindly allows me to quote his recollection of that period. He regards Rammelsberg's asperity of manner as due to his "habit of expressing himself in few words; words, however, which were always to the point, and expressed his meaning clearly." "He gave me the impression," he says, "of having a mathematical mind, and of being very accurate. His laboratory was, by comparison with those of the present date, a makeshift one; nevertheless, good work could be done there, but the appliances required for a research had, for the most part, to be extemporised. He was, however, more ready than many to adopt improved methods and apparatus. When I first went to his laboratory we had no gas, and had to use spirit lamps, and charcoal braziers for heating, but while I was there he introduced gas and other improvements; and I well remember that Mitscherlich remarked to me that so doing was a mistake, because the greater part of Rammelsberg's pupils would be dispersed in after life in places

where they could not get gas, and would find themselves in difficulty because they could not command the resources they had learnt to depend on. Another point about him was that he did his work himself. He had no assistant in research when I was with him. He had, of course, some of the more advanced students who acted as demonstrators to the younger ones, and he used the results which his pupils obtained as checks to his own work, but that work, so far as I saw, was essentially his own. How it may have been afterwards I cannot say, but I think it was in his character to be very independent, and more desirous of doing good than of making a great show. He may have been a disappointed man; his manner rather suggested that, and his way of speaking of some of his contemporaries was perhaps a little cynical."

It must be remembered that the time of which Professor Liveing writes was twenty years before Rammelsberg's labours were crowned with full recognition on the part of the university, and it is pretty certain that his rising claims for a long time met with constant opposition in Government circles. On the other hand, he was by no means a man whose efforts were directed to personal advancement, and whether he met with promotion or neglect, assistance or opposition, he was inspired by a single-hearted devotion to science, which impelled him to unremitting labour and research.

Private appreciations and reminiscences are always more impressive and trustworthy than such as are written for publication, and I am glad to have the permission of Professor Wolcott Gibbs (himself now one of our oldest foreign members), who was his pupil in 1845, to quote from a letter which he wrote to his old teacher forty years afterwards. "Many, many years have passed since I entered your laboratory as a pupil, but I well remember the pleasant afternoons that I spent with you, and the kind and friendly interest which you showed in my instruction. The very room is fresh in my mind's eye, and I remember the names of the three Greek students who were my fellow pupils. Since then, your own noble example of earnest, constant work has always been before me. Of the many noble men whom I learned to know in Berlin, you, I believe, alone remain; Poggendorf, Heinrich and Gustav Rose, Magnus, Dove, Riess, Johannes Müller, have gone. You presented me to Berzelius on the day of the dinner to him, and I sat next to you at table, when you spoke so well 'im Namen der jüngeren Chemiker.' In all these years the memory of my first teacher in analytical chemistry has always been cherished."

With reference to this occasion and the memorable visit of Berzelius, Professor Wolcott Gibbs writes to me: "Many German professors and chemists and physicists were present. Among them Jacob Grimm. Several speeches had been made, when Rammelsberg asked me how

they compared with speeches made on similar occasions in America. I told him they were admirable, but wanted what the French call *verve*, life and spirit. Then Rammelsberg rose, and made a more spirited speech, which was very well received."

His skill as a *raconteur* is vividly in the minds of those who remember those happy days of the Berlin University, when professors and students met together on terms of equality, and the latter had the opportunity of hearing the conversation of perhaps the most brilliant intellectual society in Europe. Among those who entertained each other with reminiscences in the informal evening gatherings after the meetings of the Geological Society, none could be more interesting than Rammelsberg.

His scientific character, I think, may be understood from his published works; he possessed an extraordinary industry, which was devoted to the acquisition of all possible knowledge, the addition of countless new facts to the fabric of chemistry and mineralogy, and the patient repetition and correction of any observations of others which appeared doubtful. He was singularly unbiassed by any preconceived theory, because he was singularly distrustful of all speculation, and with his industry was combined a remarkable power of accepting new views as soon as they were established, and of relinquishing his old ideas as soon as they were disproved.

His first text-book (1842) is an exposition of the electrochemical theory, and only mentions the new substitution theory of Dumas in order to reject it; but, as a matter of fact, at that date he had himself published a translation of Dumas' lectures on the Philosophy of Chemistry, and a subsequent text-book which he published (1881) is called a "Sketch of Inorganic Chemistry according to the New Views." In the preface he uses the following words: "In the subject of organic chemistry has latterly been introduced a gradual reform of the older views, based upon general principles which underlie the whole science. Those who feel with the author that the modern way of regarding the facts is a real advance, must regret that there is no introductory book available for beginners containing the elements of inorganic chemistry set forth according to the new views. The present outline, without laying claim to any merit, endeavours to supply this need. A supplementary section contains the modern laws, theories, and views so far as they relate to inorganic chemistry."

Rammelsberg was, indeed, one of the first of the chemists brought up in the old school to assimilate the new views and to disseminate them. He published a number of text-books which must have been largely used. His "Grundriss der anorganischen Chemie" ran through five editions; of his "Leitfaden für die quantitative chemische Analyse"

four editions were published; and of his "Leitfaden für die qualitative chemische Analyse" eight editions. In addition to these were published a text-book of chemical metallurgy which ran through two editions; a treatise on theoretical chemistry, one on quantitative metallurgical and mineralogical analysis, and the book already mentioned upon the new views of modern chemistry; it must be remembered that the purpose of all these books was not only to supply the student with a practical handbook, but also to give him an insight into the newer developments of the science.

Combined with his readiness to accept new ideas was an obstinate adherence to the line of work which he marked out for himself, and he never showed the least interest in the development of organic chemistry or took any part in it. His real interest was, I think, in mineral chemistry, of which he was for very many years the most prominent exponent. It is perhaps well that there was one man of untiring industry qualified to receive the torch of mineral chemistry from Berzelius and to keep it alive by his own patient researches during the fifty years when most chemists were attracted by the more dazzling discoveries of organic chemistry.

We will turn now to Rammelsberg's own work. His contributions to science are so numerous that to give an intelligible account of them within a small compass is impossible. They range over the whole domain of inorganic chemistry and mineralogy, and consist mainly of the preparation and analysis of innumerable substances, the measurement and description of innumerable crystals; references to them can be extracted from three of his books "Chemische Abhandlungen," published in 1888; "Handbuch der krystallographisch-physikalischen Chemie," published in 1881—1882; "Handbuch der Mineral-Chemie," published 1875—1895. In the endeavour to convey some impression of the magnitude and thoroughness of his work and of the extent to which the increase of chemical knowledge in the second half of the nineteenth century is indebted to his untiring industry, I shall select a few of his memoirs in chemistry, crystallography, and mineralogy respectively, and let them stand as examples of his labours —a more complete summary being obtainable in the three books which I have just mentioned.

Rammelsberg as Chemist.

In the region of general inorganic chemistry, we can take his investigations upon the halogen compounds, the phosphates, and the cyanides.

Halogen Compounds.—Many of the metallic bromides and iodides had of course been already prepared, and bromic, iodic, and periodic

acids had been discovered, but the knowledge of the iodates and periodates was very limited at the time when Rammelsberg took up their study. He prepared and analysed the bromides of barium, strontium, calcium, magnesium, zinc, cadmium, nickel, cobalt, lead, copper, mercury, and silver; the bromates of potassium, sodium, ammonium, lithium, barium, strontium, calcium, magnesium, zinc, copper, silver, lead, aluminium, cerium, lanthanum, manganese, iron, nickel, cobalt, cadmium, bismuth, uranium, and mercury.

The bromide of barium was found to contain 2 mols. of water and not 5, as stated by von Hauer; measurement of the crystals showed them to be isomorphous with the chloride.

But the most important part of the work was the study of the ammonia compounds of the bromides and iodides; these were prepared either by treating a concentrated solution of the salt with ammonia solution, or by heating the dry salt in a stream of ammonia; by the former process were prepared $ZnI_2,4NH_3$; $CdI_2,2NH_3$; $CoI_2,4NH_3$; $NiI_2,6NH_3$; $2(CuI_2,4NH_3)+3H_2O$; $ZnBr_2,2NH_3$; $CdBr_2,2NH_3$; $NiBr_2,6NH_3$; $CuBr_2,3NH_3$; by the latter process: $ZnI_2,5NH_3$; $CdI_2,6NH_3$; $CoI_2,5NH_3$; $NiI_2,3NH_3$; $2CuI_2,9NH_3$; $PbI_2,2NH_3$; $2AgI,NH_3$; $2SrBr_2,NH_3$; $CaBr_2,6NH_3$; $CdBr_2,4NH_3$; $CoBr_2,6NH_3$; $NiBr_2,6NH_3$; $CuBr_2,5NH_3$. The composition of all these compounds, their crystalline form where possible, and their behaviour on heating and on treatment with water were studied; it was shown that ammonia is liberated on heating, and that treatment with water breaks them up into hydroxides and basic salts together with ammonia, and into ammonium bromide or iodide.

The mercury compounds were found to behave differently; treatment of the solution of mercuric iodide with ammonia solution at the ordinary temperature yields a white, unstable compound, HgI_2+NH_3, identical with that obtained by the dry process, but at a temperature above 60° a brown substance is formed which is stable and is not decomposed by potash; this has the composition Hg_2INH_2O, and is analogous to the chlorine compound. The now well-known properties of this compound and its behaviour on heating were studied by Rammelsberg, who regarded it as a mercuric ammonium iodide in which 4 atoms of hydrogen are replaced by 2 of mercury.

In 1888, he returned to the study of the ammoniacal mercury compounds, when he determined anew the composition of Millon's base, studied the fusible and infusible varieties of "white precipitate," and by the direct action of acids on Millon's base prepared the mercury-ammonium sulphate, nitrate, carbonate, phosphate, bromate, iodate, and periodate.

The general investigation of bromates, iodates, and periodates belongs to his earlier research; the bromates were prepared either by

precipitation of metallic salts with potassium bromate or by solution of the oxides or carbonates in bromic acid, and yielded salts of barium, calcium, strontium, lead, mercury, and cadmium crystallising with 1 mol. of water, the copper salt crystallising with 5, and the salts of magnesium, zinc, cerium, lanthanum, nickel, and cobalt crystallising with 6 molecules of water; in addition to these, the bromates of potassium, sodium, ammonium, lithium, silver, aluminium, and mercury were prepared, also basic salts of mercury, bismuth, and uranium, while efforts to obtain the bromates of manganese and chromium were not successful. The isomorphism of the bromates of barium and strontium with the corresponding chlorates was proved by crystalline measurements. In the course of this investigation, Rammelsberg also prepared the ammoniacal bromates of zinc, copper, silver, nickel, and cadmium.

The iodates had only been previously studied by Gay Lussac and Senillas; Rammelsberg was led to their investigation by a desire to test the opinion of Gay Lussac that basic iodates of the alkalis exist. He found that this was not the case, but he proceeded to an exhaustive study of the iodates, in the course of which he prepared and studied the salts of ammonium, potassium, sodium, lithium, thallium, barium, strontium, calcium, magnesium, aluminium, cerium, manganese, iron, cobalt, nickel, zinc, cadmium, lead, tin, bismuth, copper, mercury, and silver, and several of the double salts. This included the crystallographic description of the trimorphous potassium iodate, HKI_2O_6, the double iodate and chloride of potassium, and the double iodate and iodide of sodium; it was shown that sodium iodate crystallises with 1 mol. of water above 5°, and with 5 mols. of water below that temperature; the crystalline form of the latter salt was determined, and it was found that the one substance may be converted into the other by change of temperature.

The ammoniacal iodates of nickel, zinc, and copper were also successfully prepared.

Continuing the research further, Rammelsberg made unsuccessful attempts to prepare perbromic acid and perbromates, and then turned his attention to the periodates. Periodic acid had been discovered in 1833, and a few of the salts had been examined when he took up the subject; he had already shown that among the iodates the potassium salt is the only one which is not converted into a periodate by heating, and in 1838, and again in 1869, he made a special study of the behaviour of the iodates and the periodates at high temperatures; this inquiry included the iodates of potassium, sodium, barium, strontium, calcium, and the periodates of potassium, sodium, lithium, barium, silver, and magnesium. He found that the white, infusible residue which remains after evolution of iodine and oxygen is not a

mixture of oxides, but contains iodine. With considerable difficulty (by determining the volume of the oxygen liberated), it was proved that in the case of the barium salt this is essentially the substance $R''_5I_2O_{12}$, or, as it was then called, fünftel-über-iodsaures Baryum; the existence of these compounds Rammelsberg afterwards confirmed by preparing them in other ways. The result of his laborious study of these compounds, which he made entirely his own, was to supplement, correct, and complete the work of Magnus, Ammermüller, and Langlois, and to establish the whole series of periodates $R'IO_4$; $R'_4I_2O_9$; R'_3IO_5; $R'_8I_2O_{11}$; R'_5IO_6.

The very exhaustive research upon the halogen compounds, of which the above is a very brief sketch, may be taken as an example of Rammelsberg's chemical work. He was not one of those lofty spirits who make a great discovery or are possessed by a great idea which leads them on from one intellectual triumph to another; but he was dominated by a restless zeal for research which made him quick to see the weak points in the investigations of his predecessors, and to mark the missing links in the chain of their researches. This led him at once to take up some piece of work which should either correct or confirm what had gone before, and then his untiring industry tempted him on to make the research as complete as possible.

This seems to me to have been the history of many of his investigations, and is a clue to the scientific character of the man. No difficulty was too great for him, no research was too laborious; having set his hand to the plough there was to be no turning back until the work was finished to his own satisfaction, although from a more modern point of view his limitation of the problem might often appear narrow and his vision of its possibilities circumscribed.

When we take into account that a man imbued with this spirit has worked with unceasing industry for 60 years, we should perhaps scarcely wonder that his discoveries were so numerous and his knowledge so wide. If a complete catalogue were made of the actual facts added to the store of chemical knowledge by Rammelsberg, the result would be amazing by its magnitude.

We must also remember that his independent spirit caused him always to work alone and to master every branch of his research himself. There were few men in Europe between 1840 and 1870 whose practical knowledge of chemistry and crystallography was sufficient to achieve what was accomplished by Rammelsberg.

Phosphates.—It will be sufficient to glance still more briefly at his researches upon the phosphates and the cyanides, and only in such a manner as to illustrate two other features of his character.

Having taken up a problem which was limited in itself, Rammelsberg was often led on by it from one research to another in his desire

to complete the work. This was the case with the particularly difficult work upon the phosphates.

In the course of his mineral analyses he had examined the blue phosphate of iron known as vivianite, which had always been regarded as a ferric phosphate. Rammelsberg discovered that this mineral contained both ferrous and ferric phosphate; his analysis led to the formula

$$2[3Fe_3(PO_4)_2 + 2Fe_2(PO_4)_2] + Fe_2(HO)_6 + 49H_2O,$$

but, since the crystals appear to be isomorphous with the cobalt arsenate, $Co_3(AsO_4)_2 + 8H_2O$, he concluded that vivianite was originally a ferrous phosphate, $Fe_3(PO_4)_2 + 8H_2O$, which by exposure to the air has become partly oxidised to a basic ferric salt. Rammelsberg was never content to express a view without searching patiently for all the evidence which might justify, or if adverse might lead him to modify, his opinion, and accordingly in this instance he proceeded to investigate the oxidation product of artificial ferrous phosphate, and so confirmed his theory. Its truth was still more firmly established some years later by the actual discovery in a sand at Delaware of a *colourless* vivianite which Fisher showed to be a pure ferrous phosphate corresponding exactly to the cobalt arsenate in composition. He also determined the composition of the ferric phosphate prepared from iron-alum and disodium phosphate, and showed how two basic salts can be derived from it.

In the same way, his study of the minerals wagnerite, lazulite, and amblygonite, the last-named a phosphate of aluminium, lithium, sodium, and potassium containing fluorine, which he himself regarded as one of the minerals most difficult to analyse, and whose composition he was the first to determine (1845), led him to work upon the phosphates of magnesium and aluminium. He proved the gelatinous precipitate yielded by concentrated solutions of magnesium sulphate and disodium phosphate, after washing in the cold, to have the composition $HMgPO_4 + 3H_2O$, while the filtrate yielded Graham's crystallised hydrate, $HMgPO_4 + 7H_2O$; by treatment with boiling water, the normal salt, $Mg_3(PO_4)_2 + 5H_2O$, is obtained. A study of the gelatinous precipitate obtained by mixing solutions of alum and disodium phosphate led him to the conclusion that the substance $Al_2(PO_4)_2$ may contain either 9 or 6 mols. of water.

The lithium phosphates, both mineral and artificial, were the subject of repeated research on his part; none had been quantitatively analysed with the exception of the sodium lithium salt; Rammelsberg proved the existence of the three salts $Li_3PO_4 + aq$, H_2LiPO_4, $H_5Li(PO_4)_2 + aq$. He further investigated the double salt of di- and tri-lithium phosphate, the sodium lithium phosphate, and the

lithium pyrophosphate; showed the precipitate obtained from one molecule of $Na_4P_2O_7$ and six molecules of lithium acetate to be an isomorphous mixture containing varying proportions of sodium and lithium, and found that the acid pyrophosphate, $H_2Li_2P_2O_7$, could not be obtained in a pure condition.

His investigations on the phosphites were undertaken with the object of ascertaining the basicity of the acid. H. Rose had studied the behaviour of the phosphites on heating, and (like Berzelius) had found them to have the composition $2RO,P_2O_3$, but to contain various proportions of water, the barium, strontium, and calcium salts having 2 mols., and the lead and manganese salts only 1 mol. of water of constitution, so that they were to be referred to the two acids $R_2H_4P_2O_7$ and $RHPO_3$. Wurtz, on the other hand, regarded them all as neutral salts containing 1 mol. of water. The controversy turned mainly on the composition of the phosphite of barium which Rose had found to be $H_4Ba_2P_2O_7$, while Wurtz regarded it as $HBaPO_3$. Rammelsberg repeated the analyses, and found the lead salt to be $HPbPO_3$ and the barium salt to be $H_4Ba_2P_2O_7$, thus confirming the results of Rose and Berzelius.

Having found that oxidation of barium phosphite with nitric acid yielded a mixture of oxide, metaphosphate, and pyrophosphate, he was led to investigate anew the phosphites of strontium, calcium, magnesium, zinc, manganese, nickel, cobalt, cadmium, lead, copper, and iron, especially as regards their behaviour on heating. As the result of these investigations, he concluded that there are three phosphorous acids, H_3PO_3, $H_8P_2O_7$, and H_5PO_4, derived from the union of $H_4P_2O_5$ with 1, 2, and 3 molecules of water respectively; to the first class belong the salts of potassium, sodium, ammonium, magnesium, zinc, cobalt, manganese, cadmium, lead, and copper; to the second, the salts of barium, strontium, calcium, magnesium, nickel, and zinc; and to the third the salt H_3MgPO_4. When Prinzhorn and Precht, in 1875, showed that the barium phosphite contained a certain proportion of phosphate, to which the inconsistencies were due, Rammelsberg at once gave up all these views and convinced himself that the salt really has the composition $HBaPO_3$, and that Wurtz was, after all, in the right.

He subsequently undertook the study of the hypophosphites with the view of supplementing the work of H. Rose and Wurtz, and of preparing as many of these interesting compounds as possible, especially for the purpose of a crystallographic investigation. He prepared and studied the hypophosphites of ammonium, sodium, thallium, lithium, barium, strontium, calcium, magnesium, zinc, manganese, cerium, cadmium, lead, cobalt, nickel, and uranium, and compared their isomorphous relationships where they exist.

When it is remembered that in this and many similar pieces of work Rammelsberg spared no pains in preparing, not only material for analysis, but also crystals which could be crystallographically studied with all the means at his command, and that the whole work of measurement and calculation was done by himself, one may well be surprised that even in his long life of activity so many of these researches were carried out.

Cyanides.—If our knowledge of the halogen compounds and of the phosphates, phosphites, and hypophosphites is largely derived from the labours of Rammelsberg, still more is this the case with the double cyanides. His work upon these began with his inaugural dissertation in 1837, of which the purpose was to complete the work of Gmelin, Wöhler, and Ittner by the preparation of the potassium and cadmium double cyanides.

It is scarcely necessary to recapitulate the long series of compounds which he prepared; they have become a part of the edifice of inorganic chemistry, throughout the whole framework of which the handiwork of Rammelsberg is to be traced by those who care to look up the authorities for the accepted facts of the science.

A large portion of the work was devoted to the behaviour of cyanides and double cyanides at higher temperatures, to which he was led by Thaulow's discovery of paracyanogen and his work upon the decomposition of cyanide of silver by heat. He repeated these experiments and found that the so-called carbazote, obtained by heating cyanide of silver, differed in no respect from cyanogen; his further experiments upon the double cyanides were chiefly devoted to the determination of the nature of the distillation residues obtained on heating.

Upon the subject of the double cyanides, Rammelsberg held very decided views, and expressed himself as strongly opposed to the ferrocyanogen theory of Porret and Liebig. His position is perhaps best stated in his own words, which will serve to illustrate the clear and direct character of his statements, and also, perhaps, the prejudices by which his views were limited:

"According to the ferrocyanide theory, Prussian blue is not $3FeCy_2+2Fe_2Cy_6$, but $Fe_4,3FeCy_6$. Gmelin's blue is not $3FeCy_2+Fe_2Cy_6$, but Fe_3,Fe_2Cy_{12}."

(Rammelsberg always in his teaching preferred to use the name "Gmelin's blue" in place of "Turnbull's blue.")

"Now, as is well known, there are two other compounds, namely:

"(1) $KCy+FeCy_2$, which is separated when yellow prussiate of potash is heated with dilute sulphuric acid. According to the ferrocyanide theory, it would be treated as $K_4,FeCy_6+Fe_2,FeCy_6$.

"(2) $KCy+2FeCy_2$, the red precipitate obtained from potassium cyanide and ferrous salts, which was investigated by Städeler. If it is treated as K,Fe_2Cy_5, a third radicle must be assumed. The adherents of the ferrocyanide theory maintain that all double cyanides fall into two classes:

"A. Simple haloid salts of a substance consisting of cyanogen and a metal. To this class belong the series $4KCy+RCy_2$, and the series $6KCy+R_2Cy_6$, and also from the series $2KCy+RCy_2$, the platinum and palladium compounds. In these the following radicles must be assumed:

$$RCy_4\ ;\ RCy_6\ ;\ R_2Cy_{12}.$$

"B. Double salts. This includes the remainder of the series, $2KCy+RCy_2$, and also the salts of gold, silver, and copper.

"But why should this difference of constitution be assumed?

"The salts of the first class (we refer in particular to the potassium compound) yield in solution with dilute acids at ordinary temperatures no prussic acid, as do those of the second class.

"The reason why the former apparently suffer no decomposition is to be found in the formation of a corresponding hydrogen compound.

"This action of acids, however, is limited to a portion of the salts. Whilst yellow and red prussiate obey the rule, and potassium cobalt cyanide behaves in the same way, my experiments show that the solution of potassium manganese cyanide, which decomposes of itself with liberation of manganese oxide, yields prussic acid freely with acids, and the same is true of potassium chromium cyanide. The hydrogen compounds prepared from the corresponding salts liberate hydrogen cyanide freely when their solutions are heated. The ferrocyanide theory assumes that here $H_4,FeCy_6$ is converted into $4HCy$ and $FeCy_2$.

"The potassium salts of ruthenium and osmium are also decomposed by acids with formation of the hydrogen compounds, whose solutions quickly liberate prussic acid and deposit $RuCy_2$ and $OsCy_2$.

"How different may be the behaviour of analogous and isomorphous salts towards acids is illustrated by $K_6Ir_2Cy_{12}$, which behaves like the red prussiate, while $K_6Rh_2Cy_{12}$ yields prussic acid and Rh_2Cy_6.

"Hence the action of the cyanogen compounds with acids is not a sufficient reason for assuming two classes of different constitution. Their liability to decomposition varies greatly, and is weakest in the iron compounds.

"Closely related to the behaviour of the double cyanides towards acids is their physiological action. But to adduce this action, which is limited to the experiment with potassium iron cyanide, in support of the ferrocyanide theory is wholly unjustifiable, for the physiological action of a chemical compound does not depend upon the nature and association of its elements.

"If now the behaviour of the double cyanides towards acids is not such that it implies a difference in their constitution, but only indicates a more or less intimate union of the two components, which, in the compounds of zinc, cadmium, copper, &c., is admittedly so weak that the precipitates yielded by the potassium salt with other metallic salts are either of a different composition or merely mixtures, then the only support for the hypothesis of a ferrocyanide and other metallic radicles falls to the ground.

"The behaviour of the double cyanides towards hydrogen sulphide or alkaline sulphides, the impossibility of precipitating the iron as sulphide from

prussiate of potash, which is adduced by some as a further support of the ferrocyanide theory, is based upon an almost incredible ignorance of the facts.

"It has long been known that potassium cyanide dissolves many of the metallic sulphides with production of potassium sulphide, $6KCy + FeS = 4KCy + FeCy_2 + K_2S$. It is therefore self evident that alkaline sulphides cannot precipitate sulphide of iron from prussiate of potash."

It is easy now to see how Rammelsberg failed to appreciate modern distinctions between double salts and salts of complex acids. I think that even his later papers take no account of contemporary work upon electrolytic dissociation. Neither did he pay any attention to the important aid afforded by the complex cyanides in the periodic classification of the metals, especially the Fe, Co, Ni, and Pt group. And similarly in the halogen compounds there is no evidence that he would have attached much importance to the use made of the salts of silver bromide with ammonia in developing the theory of dissociation by Joannis and Crozier and others. But, perhaps, this is unfair anticipation, for his own researches belong to a much earlier period.

Among the other large contributions to general inorganic chemistry must be mentioned Rammelsberg's researches upon the sulphantimonates; he was the first to determine the composition of Schlippe's salt, and to prepare and study a great number of these compounds, and the potassium antimonyl sulphantimonate was of special interest 60 years ago as the first instance of a double salt whose constituents have the same electropositive element; he also undertook a laborious repetition of Rose's work upon tantalum and niobium, which had been called in question and partly disproved by Marignac and Blomstrand, so that a complete revision was necessary in order to confirm what was right and to eliminate what was wrong. In Rammelsberg's own words: "It seems an irony of fate that H. Rose, the discoverer of the volatile oxychloride of chromium, who proved that the supposed superchlorides of molybdenum and tungsten are oxychlorides, should himself have taken niobic oxychloride for niobic chloride (Unterniobchlorid). Similarly, as is well known, Berzelius took the vanadium oxychloride for vanadium chloride, as was first proved by Roscoe. Of Rose's results, all that relates to his Unterniobsäure is correct, but his niobium compounds were mixtures, and his tantalum compounds were not free from niobium. Rose's memoirs are to be found in Poggendorff's *Annalen*, volumes 63—113. I have extracted from them all that is firmly established both now and for the future of the science (*ibid.*, 136, 177)." Mention only can be made of Rammelsberg's researches upon ozone, upon the hyposulphites, the sulphites, nitrosulphonic acid, the nitrites, titanic acid, the vanadates, the phosphomolybdates, the salts of uranium, of thallium, of cerium, and of lithium, and his determination of the atomic weights of

molybdenum, cerium, lanthanum, uranium, and of the metals of the yttrium group. In the last-mentioned he strongly opposed the view of Nordenskiöld that the atomic weight of these metals is nearly constant in the minerals which contain them.

One of his important papers was communicated to this Society, "Experimental Researches on the Amalgamation of Silver Ores" (Trans., 1881, 39, 374). Being engaged upon a translation of Percy's metallurgy into German, he was struck by the very imperfect experiments which had been made with the object of discovering the chemical changes which take place in the Mexican amalgamation or Patio process. With characteristic energy he made it his first business to repeat and extend these experiments, and to obtain for the first time quantitative results. He studied the action of cuprous and cupric chlorides on silver chloride, sulphide, arsenide, sulpharsenide, and sulphantimonide, and although it cannot be said that his experiments dispelled the mystery that surrounds the Mexican process, they supplied for the first time numerical data on which the explanation of that process must be based.

One of the most unintelligible features of Rammelsberg's scientific work has been alluded to above, and must be again noticed. During the period when the whole science of chemistry was being transformed by its development on the organic side, Rammelsberg, almost alone, remained steadfastly immersed in inorganic research, and was never tempted into the attractive region of the carbon compounds. With the exception of a few isolated researches, mostly of a crystallographic nature, his work upon the oxalic acids and their salts and upon the uranium acetates are the only important investigations which carried him across the borderland, and these are almost entirely of crystallo-chemical interest.

It was not that he closed his eyes to the extraordinary development of organic chemistry, or failed to make use of its teaching; indeed the subject is adequately treated in his own text-books, and, as I have pointed out, he was one of the earliest adherents of the new chemistry; but he purposely confined himself to a path which he had marked out at the beginning of his career, except where his own researches led him to make temporary excursions into the region of allied subjects.

Rammelsberg as Crystallographer.

In 1801 Haüy had written that "at the École des Mines, chemistry and crystallography, so long separated, had entered into a close partnership which they have promised never to dissolve." No one contributed more to the maintenance of this partnership than Rammelsberg.

Of his own work on the acetates, he says: "The previous data con-

tained so many contradictions that, evidently, the material which was analysed and the material which was measured cannot always have been the same. A work carried out along both lines has removed all the doubt and error which resulted from the fact that the chemist did not measure the salts which he analysed, and the crystallographer did not analyse the salts which he measured."

For example, he showed in this paper that two manganese uranyl acetates crystallise out in succession from a mixed solution of the acetates, and that the measurements of Grailich had been made upon one of these, and the analysis of Weselsky upon the other; they had, of course, been supposed to relate to the same substance.

It is painful to reflect how often this sort of thing may have happened during the nineteenth century, and the reproach against chemists that they lack a practical knowledge of crystallography, and against crystallographers that they lack a practical knowledge of chemistry, is by no means removed. It is, however, a hopeful sign of the times that a younger school of chemists is now rising against whom this reproach can no longer be brought.

Even in 1881 Rammelsberg could use the following words on the subject ("Handbuch der krystallographisch-physikalischen Chemie," preface):

"Physicists and chemists meet in a region which stimulates the research spirit of both. Has not specific heat acquired a great importance for chemistry? Has not the electrolysis of compounds exercised an effect upon the views of pure chemistry? Have not spectroscopic phenomena been transferred from the domain of optics to that of practical chemistry? The chemist sees himself continually driven to the study of physical phenomena. . . . The chemist must investigate the geometrical and other physical properties of substances as well as their composition and reactions. . . . If, however, we compare our chemical handbooks with the mineralogical, we cannot fail to notice the very unequal treatment which the individual properties receive. For each mineral is given a special description of the crystalline form; *i.e.*, the constants obtained by observation and calculation. . . . The handbooks of chemistry, even the more complete, treat the most important physical properties either in a fragmentary manner or not at all. This is true of the crystalline form, the optical characters, the expansion, specific heat, electrical and magnetic properties; the reader is left to seek the physical constants of a substance in physical treatises or journals. Leopold Gmelin's great work alone takes due account of the crystallographic elements.

"A result of this neglect of the physical properties in our chemical textbooks is the incompetence of young chemists to investigate their own preparations crystallographically and optically. And yet it is not so difficult to acquire the requisite crystallographic and physical knowledge, instead of leaving this investigation to others. In a precisely opposite manner the mineralogists formerly erred by confining themselves to the geometrical and physical properties, and neglecting the chemical, so that we learnt from them what a

mineral looks like but not what it is. A substance bearing the same name, but analysed by another man in another place and at another time, was often an entirely different mineral. Such a division of labour frequently leads to blunders ; an instructive example is afforded by the memoir of Schabus, which was crowned by the Vienna Academy of Sciences (in 1855). In this, potassium lithium sulphate is described as lithium sulphate, the sulphates of didymium and lanthanum are described as the chlorides, under the name grape-sugar is described the compound with sodium chloride, &c."

One of Rammelsberg's great books of reference, from the preface of which the above is quoted, was designed to supply the need of which he complains, and to give chemists a book in which they could find precisely what was wanting in their own treatises. With immense labour he collected for this book all the crystallographic, optical, and other physical constants of all the crystallised compounds which had been described, adding full references so that the reader could always turn to the original sources. It was, and is still, an invaluable book of reference, although, of course, the volume dealing with organic compounds is now quite inadequate, owing to the rapid accumulation of facts during the last 20 years ; it would no longer be possible to include all the physical as well as the crystallographic characters of chemical compounds in a single volume of reasonable dimensions ; and the modern method of treating the former in separate works is, no doubt, more convenient.

To the crystallographic knowledge of chemical compounds no man contributed more largely than Rammelsberg himself. Without his labours, the illuminating discovery of isomorphism would never have exerted such widespread influence, and no man was better fitted to carry on the work of his great master, Mitscherlich.

In crystallography as a distinct science, Rammelsberg had, I think, no particular interest ; he regarded it only as a means to an end. Born only four years after the discovery of the reflecting goniometer by Wollaston, he became one of the most practised experts with that instrument, and regarded it as part of the armoury of the chemist.

His student days were set at an interesting time in the history of the young University of Berlin. The Abbé Haüy, the real founder of crystallography, was still alive, and the science had made rapid advances in the hands of German and English investigators. Weiss had recently introduced the use of axes to which the faces of a crystal can be referred and which suffice for its description ; he and Mohs had independently established the existence of the six systems ; the laws of the double refraction of crystals belonging to these different systems and the methods by which they can be studied had been elaborated by Brewster and Herschel. In no place could the newly

developed science be better studied than in Berlin ; Mitscherlich was Professor of chemistry, Weiss of mineralogy, and Gustav Rose had recently (1822) been appointed ausserordentlicher Professor of mineralogy.

Rammelsberg worked with all these men, and his whole scientific career was determined by their inspiration, but he always remained content with the crystallographic methods of his student days, and was satisfied if he could determine the form of every crystallised compound which he prepared and express it in the manner which had become familiar to him in 1834. Weiss called the three axes of a crystal *a b c*, and denoted any face by its intercepts on these axes by means of a symbol such as $[ma, nb, pc]$. Rammelsberg always employed this notation ; Neumann in 1823 had already introduced the convenient method of denoting the faces of a crystal by their normals and by the points in which they intersect a sphere, and Whewell in the same year had suggested the use of indices, afterwards developed by Miller, according to which a face whose intercepts on the axes are $\frac{a}{3}, \frac{b}{2}, \frac{c}{4}$ is denoted by the symbol (324) ; yet he would not even adopt the notation of Naumann, which became almost universal in Germany. He says in 1881 "I have used the notation introduced by Weiss, the founder of the new crystallography, because I regard it as in itself better than any other, and I employ the actual angles between the faces because they alone, and not the angles between the normals, are expressed by the crystal itself. It is certain that the study of crystals would have been much more widely diffused among chemists if crystallographers had followed neither Naumann nor Whewell and Miller."

This was a curious piece of conservatism which would hardly have been expected on the part of one who, as we have seen, was so quick to absorb new views in chemistry and to change his position in conformity with the advance of that science. Having regard to the rapid displacement of Weiss's system by Naumann's, and the present almost universal acceptance of Miller's notation, it is easy to see that this adherence to an antiquated notation was one of the chief causes which prevented his book from becoming more widely known. For this reason, also, it is probable that two elementary text-books of crystallography for chemists, which he published in 1857 and 1883 respectively, never had a wide circulation, although they are written with admirable lucidity.

None the less is the Handbook an invaluable storehouse of useful information, and none the less were Rammelsberg's own contributions to chemical crystallography of immense importance. Let us, without entering into details, glance at a few of his investigations. Among

those of most general interest are his work upon the isomorphism of sulphur and selenium, and of the compounds of vanadium and phosphorus.

From experiments on the density and the solubility of selenium, Rammelsberg concluded that there are three, and not two, crystalline modifications of this element, in addition to the amorphous variety. Mitscherlich had measured crystallised selenium with great care, but found its form to be different from that of sulphur ; Rammelsberg showed that the crystals obtained from solution in carbon disulphide are probably isomorphous with the monoclinic variety of sulphur, and this conclusion was afterwards confirmed by vom Rath, who found that isomorphous mixtures of the two elements possess sometimes the form of orthorhombic, but sometimes the form of monoclinic sulphur, proving that a monoclinic modification does enter into such mixtures. He subsequently endeavoured to prepare the potassium tellurate which had been described as isomorphous with the selenate and sulphate, but found no justification for the suggested isomorphism of tellurates with selenates. The isomorphism of sulphur and selenium has since been the subject of research by Muthmann, who has established the crystallographic relationships between these elements so far as they are at present known, and he is not disposed to accept the isomorphism of the selenium crystals here alluded to with the ordinary monoclinic sulphur, although it may occur with another monoclinic modification.

In 1856 Rammelsberg pointed out that the mineral vanadinite, the chlorovanadate of lead, in which vanadium was first discovered, is undoubtedly isomorphous with pyromorphite, the chlorophosphate, and insisted that the isomorphism must imply an analogous formula, especially since vanadinite contains some phosphoric acid, as he found by the analysis of specimens from Carinthia. At that date, the views that were held concerning the constitution of vanadic acid did not render this interpretation possible, and Rammelsberg declared that this must either be a case of the isomorphism of substances which are not similar in constitution, or else vanadic acid is not VO_3, but V_2O_5, hereby predicting the result of Roscoe's classic work.

From what has been already said, it will be understood that, among the bromides, bromates, iodides, iodates, and periodates, the phosphates, phosphites, &c., and the cyanides, the isomorphous relationships of many series of salts were established by Rammelsberg ; the same is true of the double chlorides, such as $2R'Cl + R''Cl_2 + aq$; the dithionates ; the arsenates, &c.

Among the phosphates, he showed that H, K, Am, Tl replace one another in isomorphous salts. Among the uranyl double acetates he traced three series in one of which manganese is replaced by cadmium, and in another by magnesium, whilst in the third magnesium is replaced by zinc, nickel, cobalt, or iron ; the barium, strontium, and calcium

series, containing 2 atoms of uranium and 6 mols. of water, constitute another isomorphous series, whilst in the alkali series potassium may be replaced by silver. Among the sulphates, he contributed cases of the isomorphism of yttrium, erbium, didymium, and cadmium, and of uranium with thorium.

Many of these researches bore upon the isomorphism of compounds containing the alkali metals. He was the first to establish (in 1853) the tetartohedral character of sodium chlorate by observing that a cube of this substance might have only four faces evenly replacing its corners and twelve faces unevenly replacing its edges; he was also the first to make crystalline mixtures of cubic sodium chlorate with tetragonal silver chlorate; his preparations were afterwards used by Lehmann and served to demonstrate the fact that silver chlorate is dimorphous. He established also the dimorphism of manganese chloride, and proved the isomorphism of tin, platinum and palladium in the double chlorides. The polymorphism of tin itself was the subject of a special investigation in which he studied in particular the transformation of ordinary into gray tin and came to the conclusion that there are three modifications of this element, and that gray tin may become transformed below its temperature of fusion into tetragonal and perhaps also into ordinary tin; in this connection, the alterations which take place in the alloy used in organ pipes after continued use, possibly due to vibration, are of interest. He measured crystals of an alloy of tin and copper which proved to be hexagonal, and adduced strong reasons for regarding many other alloys such as those of copper and zinc, gold and tin, iron and tin, tin and antimony, gold and antimony, gold and mercury, as mixtures of isodimorphous substances.

His early experiments on the solubility of mixed sulphates (in 1854) were the first observations of this sort, and were the beginning of a class of research which has subsequently, in the hands of Bakhuis Roozeboom and others, led to such fruitful results. In these and kindred researches, Rammelsberg may be regarded as one of the pioneers of modern physical chemistry. He was the first to suggest a principle which has since been elaborated by Wyrouboff and others, that the axial ratios of the substances which are capable of forming mixed crystals are not necessarily almost identical, but may bear a simple rational relation to each other; the possibility of isomorphous substances presenting almost identical angles in some zones of crystal faces whilst differing considerably in others is brought out in his study of the phosphates of ammonium, thallium, and sodium.

The most interesting of his memoirs on these subjects, and, considering the date at which it was published (1854), the most remarkable, was that already referred to upon mixed crystals of the sulphates of the series $R''SO_4,7H_2O$. He found that the crystals obtained by

fractional crystallisation do not possess the same composition as the solution from which they crystallise, if the solubility of the constituent salts is not the same, but that successive crops are produced of which the last contain a greater proportion of the more soluble salt; he also showed that in some of these cases the mixed crystals are only capable of forming within certain limits, and that an excess of one constituent may crystallise out in a pure condition beside the crystals of mixed constitution; further, that in such mixtures, for example, as those containing iron and magnesium, the crystals possess the rhombic form of magnesium sulphate when Mg : Fe is greater than 3, and the monoclinic form of the ferrous sulphate when Mg : Fe is equal to or less than 1.

At that date, such mixed crystals were usually supposed to be mere parallel growths consisting of alternate layers of the two constituents; Rammelsberg made it very clear that their complete homogeneity and their optical properties proved them to be really molecular mixtures. In this very important work, he was opening up a line of research which leads directly to all that has since been done upon the properties of solid solutions, and induces me to repeat that Rammelsberg, although he has not received the credit for it, was certainly one of the pioneers in modern physical chemistry.

It is not necessary to pursue this subject further; it is now familiar to all chemists, and an admirable summary of the subsequent work is to be found in the English translation of Fock's "Introduction to Chemical Crystallography."

One striking result of Rammelsberg's work on the mixed sulphates deserves notice; his analyses of the mixed sulphates led him to the conclusion that, in some of these at any rate, the mixture does not take place in arbitrary proportions, but only in certain fixed molecular proportions; in other words, that they are of the nature of double salts, although their properties may be indistinguishable from those of a mixture. Since the publication of Dufet's research, which indicated a continuous change of the geometrical and physical properties as the composition of the mixed zinc–magnesium sulphate changes, this result has been ignored; but Rammelsberg was a careful observer, and his experiments ought to be repeated.

I have perhaps now quoted enough of his crystallographic work to show what valuable results he was able to obtain by his familiarity with the use of the goniometer, and his recognition of the fact that this instrument should form part of the equipment of a chemist.

Of the all important work relating to isomorphism that formed so large a part of Rammelsberg's labours, the greater portion lies in the field of mineralogy, where his contributions to science were even more

extensive than the chemical and crystallographic researches which we have just surveyed.

Rammelsberg as Mineralogist.

In attempting now to form an estimate of Rammelsberg's labours, which have long become a part of the scientific heritage of the present generation, we must continually bear in mind that, although he died in 1899, he was beginning to publish in 1837, and it is necessary to picture to ourselves the condition of science at that date. This is true of his chemical and crystallographic work, and it is equally true of his mineralogical memoirs in which both chemistry and crystallography are combined. Fortunately, it is easy to get a picture of the condition of mineralogy at different periods in his career, for the standard text-book was the work of his exact contemporary, Professor James Dwight Dana, and the successive editions of that book reflect accurately the successive stages of the science. The first edition was issued in 1837, the very year in which Rammelsberg's first work was published; the sixth edition, edited by Professor Edward Dana, was issued in 1892, when Rammelsberg had just resigned his professorship; the immense difference between the two in their chemical aspect is really an eloquent testimony to the influence of his work.

In 1837, mineral chemistry did not exist except in the mind of Berzelius, and perhaps of one or two of his followers. In the first edition of Dana's mineralogy, not a single formula is given, and in the preface the following remarkable statement occurs: "When the crystallisation of a species is sufficiently distinct to serve as a guide in distinguishing species, the results obtained by chemical means should never modify the decisions of the mineralogist," and, subsequently, after it has been confessed that chemical and blowpipe tests are often a valuable assistance, "in making this admission it does not appear that we degrade the science of mineralogy from its rank among the natural sciences as some of its most distinguished authors would affirm."

That a mineralogist should have to apologise for analysing a mineral, and regard an analysis as a degradation to his science, seems now scarcely credible, but so it was in 1837. It is true that some glimmering of the influence of Berzelius may be discerned in the shape of a little appendix on chemical classification. Minerals, it is there said, may be classified either by their electropositive or by their electronegative elements; the latter is perhaps preferable, for Mitscherlich's principle of isomorphism has shown that the electropositive elements may replace each other without introducing any change into the physical characters. On the other hand, later discoveries indicate

that the electronegative constituents may also replace each other; so that on the whole there is an objection to any chemical classification whatever.

The second edition appeared in 1844. Here the classification adopted is that of Mohs—the latest refinement of the so-called natural-historical system of Werner—in which the species are defined by their external characters alone, especially the hardness and the specific gravity, and not by their composition. The species are grouped into genera, and the genera into orders, and they all receive Latin names like those used for plants.

In this second edition, however, the appendix on chemical classification contains a survey of the mineral kingdom in which the species are arranged solely by their chemical constitution, and are defined by chemical formulæ. The secret of this change is explained by the author himself; he says, "The very elaborate treatise on chemical mineralogy by Rammelsberg, which has lately appeared in Germany, has afforded nearly all the materials for this part of the table."

It will be found that at this date, over seven years after he had began to publish, Rammelsberg is already responsible for no less than 56 of the formulæ, and in succeeding editions his influence is no less strongly felt. In the third edition of Dana, the natural history system is thrown over, and the classification becomes mainly a chemical one, and nearly identical with that adopted at the present day.

This transformation of mineralogy was, of course, originally due to Berzelius; its beginnings are sketched in Whewell's "History of the Inductive Sciences," where it is treated as an almost contemporary episode.

Berzelius had first, in 1816, proposed a classification of minerals according to the electropositive elements, and subsequently, when this had been subjected to much criticism and was found to be incompatible with various isomorphous relationships, he replaced it by an arrangement mainly according to the electronegative elements.

No one interested himself more in the dissemination of the views of Berzelius than his friend Rammelsberg, who published in 1847 a small volume containing translations by Gmelin, Pfaff, and himself of seven memoirs by Berzelius relating to the classification of minerals. Two of these are the schemes just referred to, the others are replies to his various critics, and the volume closes with a paper by Rammelsberg himself, a survey of the mineral kingdom upon the lines laid down by Berzelius.

In a preface, he remarks "According to this principle the different augites, hornblendes, garnets, &c., which contain different bases cannot be placed together. But whatever may be the objections to

the chemical system from the purely mineralogical standpoint, it cannot be denied that it is based upon a single principle, and that this can be conveniently carried out through the whole scheme."

It was, I think, characteristic of the man that he did not devote any more time to the academic discussion of the principles of classification —in his own first treatise the minerals were arranged by the most convenient of all methods, an alphabetical order—but, having convinced himself that a chemical system would be possible, he set to work upon the analyses without which any such classification would be premature.

The treatise was entitled "Handwörterbuch des chemischen Theils der Mineralogie," and was published in 1841; it was dedicated to Heinrich and Gustav Rose. The book contains all the mineral analyses at that time published, including a number of new analyses by Rammelsberg himself, and gives the reactions and blowpipe tests for each species. All the formulæ are calculated from the atomic weights of Berzelius, and the theoretical composition of each mineral is given. A few pages of introduction give the principles of mineral chemistry as laid down by Berzelius, and the method of calculating formulæ.

The book was welcomed with acclamation by Berzelius, Leonhard, Kobell, and the other leaders of chemical and mineralogical science. In his Jahresbericht for 1843, Berzelius gives the following appreciation of the work:

"Mineralogy has been enriched by a work of the highest value to those who believe that the study of the chemical composition of minerals belongs to this science. The minerals are arranged in alphabetical order and all their known analyses are given, accompanied by a profound criticism of the analytical methods employed therein, together, often, with a recalculation and the requisite correction of the results deduced. It fulfils two requirements which are seldom simultaneously satisfied, it is exhaustive without being wearisome by excessive elaboration. The introduction contains a brief but clear and systematic representation of the chemical constitution of minerals, and the way in which they are to be criticised according to the results of the analyses.

"Seldom has a book been so much needed or so well supplied the need. The industrious author deserves the greatest thanks for his useful and laborious undertaking."

Between the years 1843 and 1853, five successive supplements were issued at intervals; not only did these contain all the new analyses which had been published, but the composition and formulæ were all recalculated with the corrected atomic weights.

It will by this time be suspected from what has gone before that most of Rammelsberg's life was devoted to the laborious accumulation of new facts, and that he did not publish much of a speculative nature or enter into the wordy strife of scientific controversy; he was content

to criticise and correct by the quiet process of experiment and observation.

Each of these supplements to the Handwörterbuch contains a general introduction which gives a clue to what he considered most important and interesting in contemporary mineralogy and to his own opinions on controversial subjects.

For instance, in the second supplement (1845), he explains that Gmelin had accepted SiO_2, in place of SiO_3, as the constitution of silica. The formulæ of most of the important silicates on this hypothesis are given, and Rammelsberg confesses that many are considerably simplified, but the principle is not yet accepted.

The third supplement (1847) contains a notice of Wallmark's suggestions concerning silicates of the monoxide bases, namely, that in these, whatever may be their differences of system, two of the crystallographic axes bear nearly a constant ratio 0·92 : 1. The recent investigations which led to the detection of phosphoric acid and fluorine in very many minerals, and Ebelmen's work on the decomposition of silicates, are also noticed.

In the fourth supplement (1849), the recently suggested possibility of the isomorphism of sulphur and arsenic compounds is discussed, and Rammelsberg thinks it cannot be maintained.

The relationship between the rhombic bournonite ($PbCuSbS_3$) and the hexagonal red silver (Ag_3SbS_3), which had been compared by Gustav Rose to that between aragonite and calcite, is in his opinion due to proportionality of atomic volumes.

$$\frac{\text{Calcite}}{\text{Red Silver}} = \frac{232}{1180} = \frac{1}{5}\ ;\ \frac{\text{Aragonite}}{\text{Bournonite}} = \frac{214}{1073} = \frac{1}{5}.$$

The greater part of these introductions, however, is devoted to a criticism of Scheerer's polymeric isomorphism and of Hermann's heteromerism ; it is difficult now to appreciate the importance which these theories assumed in the eyes of their contemporaries, and it is almost forgotten how large a part was played by Rammelsberg in their demolition. In Ernst von Meyer's "History of Chemistry," Rammelsberg is dismissed in a paragraph (he is also killed before his time), and the Hermann—Scheerer controversy is scarcely discussed ; and yet these views must have, for a time, held the field masterfully. In his fourth supplement, Rammelsberg prefaces his criticism with the remark "The criticism of Scheerer's and Hermann's theories may, it is hoped, induce others to express their opinions openly." Scheerer, it will be remembered, believed that in many silicates and other minerals RO may be replaced by $3H_2O$; his argument relied chiefly upon the mineral aspasiolite, which has the form of cordierite, and also a similar composition if 1 mol. of magnesium oxide may be regarded as replaced by

3 mols. of water. The serpentine crystals from Snarum in Norway were supposed to be another example. Rammelsberg insisted that aspasiolite and the allied minerals are only altered cordierite which has gained water during decomposition (the mineral has subsequently, owing to the work of Haidinger, Naumann, and others, been deposed from its high position, and is now known to be certainly a pseudomorph after cordierite); Rammelsberg also showed that the minerals of the scapolite group upon which also Scheerer largely relied are particularly liable to alteration. The arsenate of cobalt, according to Scheerer, contains 6 mols. of water, and its isomorphism with the ferric phosphate, vivianite, is only brought out by assuming that FeO is replaced by $3H_2O$; Rammelsberg insists that both minerals contain 8 mols. of water. Scheerer's further hypothesis that CuO can be replaced by $2H_2O$, and $2SiO_2$ by $3Al_2O_3$, he stigmatises as entirely arbitrary.

Hermann's heteromerism, which has also passed into the limbo of forsaken theories, and is dismissed by Arzruni in his volume on the physical chemistry of crystals in Graham-Otto's Lehrbuch as of no importance, was criticised by Rammelsberg with great care, and I think will be found on examination to be far less alien to modern views than is commonly supposed. The real hypothesis of Hermann was that substances of nearly the same form, but quite different composition, can mix to form homogeneous crystals; epidote, for example, is a mixture of the two following compounds:—

Zoisite..... $\dot{R}_3\dddot{S}i + 2\dddot{R}\dddot{S}i$

Bucklandite ..... $2\dot{R}_3\dddot{S}i + 3\dddot{R}\dddot{S}i.$

That substances of different composition may have nearly the same form Rammelsberg confesses; that they can enter into isomorphous mixtures he regards as not proven, but contents himself with the principle. "Substances which have nearly the same crystalline form possess the same or proportional atomic volumes."

The fifth supplement (1853) gives evidence of the rapidly extending acceptance (due largely to Dana and Kobell) of Kopp's idea that the isomorphism of minerals depends upon the equality or proportionality of their atomic volumes. Rammelsberg himself at that date regards

Tourmaline as $\dot{R}_3\dddot{S}i_2 + n\dddot{R}\dddot{S}i$ with $\dot{R}\dddot{S}i + n\dddot{R}\dddot{S}i.$

Felspar as $\dot{R}_n\dddot{S}i + n\dddot{A}i\dddot{S}i_n.$

Mica as $n\dot{R}\dddot{S}i + n\dddot{R}\dddot{S}i.$

Hornblende as $n\dot{R}\dddot{S}i + n\dot{R}_3\dddot{S}i_2.$

These are all instances of the multiplying cases of isomorphism among compounds which differ in the number of their atoms.

From that day to the present time, mineral chemistry has been mainly occupied with the endeavour to discover the isomorphous constituents which mix to form a mineral of complex composition such as tourmaline or epidote; that they are isomorphous mixtures is, of course, firmly held, but the proportionality of atomic volumes is no longer invoked as a criterion, and similarity of composition is now so liberally interpreted that the views of Hermann should no longer be dismissed as wild speculations.

In many of the questions concerning which controversy raged, such as whether only the constituents which enter into the mixtures are to be called mineral species, or whether the intermediate mixtures also deserve that name, Rammelsberg took little or no interest. His business was to supply the solid foundation of fact only to be attained by laborious analyses, upon which alone theory can be based.

In my opinion, the most important contributions which Rammelsberg made to science were those which he made as a mineral chemist. If, as we have seen, he brought to the study of chemistry a much needed knowledge of crystallography, he certainly brought to the study of minerals an even more needed knowledge of chemistry.

He himself deplores the fact that in the early days of the science Haüy was solely a crystallographer and Klaproth a chemist. "What rapid strides would have been made by mineralogy if Haüy's crystallographic knowledge and Klaproth's chemical ability had been united in a single person." It is not often that a science suffers from over specialisation in its early periods, but the study of minerals is not so much a distinct science as a region in which three sciences meet, and few were gifted with the power of mastering all three. No man was better equipped than Rammelsberg to achieve conquests in this unexplored region. His published papers on mineralogical subjects are very numerous (including those on rocks and meteorites, about 300); their results are incorporated in his great treatise, "Handbuch der Mineralchemie," which succeeded the "Handwörterbuch," already mentioned. The first edition of the "Handbuch" was issued in 1860, the second edition in 1875, an "Ergänzungsheft" in 1886, and a second supplement in 1895. Rammelsberg's mineralogical work is so vast that here again in order to form an estimate of its character I propose to select only two or three examples, and to leave his "Handbuch" to describe the remainder.

Augite and Hornblende.—Conspicuous among his early papers are those on the augite and hornblende group of minerals. These two minerals were only distinguished by their cleavage angle and form. Augite was known to be a "bisilicate of lime and magnesia in which part of the bases is replaced by protoxide of iron and part of the silica by alumina"; hornblende was almost the same, "the analyses only

prove that augite usually contains more lime, less alumina, and no hydrofluoric acid, which is peculiar, though in minute proportions, to hornblende" (Allan's "Mineralogy," 1834, p. 149). Augite was made to include the minerals known as augite, diopside, baikalite, fassaite, coccolite, sahlite, and omphacite; hornblende included the species known as hornblende, actinolite, tremolite, asbestos, hedenbergite, and pargasite.

Gustav Rose had proved that augite and hornblende may be referred to the same crystal axes, and urged that they may therefore be regarded as the same mineral; it is true that they have a different cleavage angle, and that the faces that occur upon the one are not found upon the other, so that they present quite a different aspect, but they are sometimes found attached to one another in parallel positions; further, Rose showed that when hornblende is fused, it recrystallises as augite; it was therefore supposed that the temperature at which the mineral was formed may have been sufficient to determine whether it should crystallise with the faces and cleavage of augite, or with the faces and cleavage of hornblende.

Subsequently, Rose himself discovered that a mineral, to which the name uralite was given, possesses the faces of augite and the cleavage of hornblende, and is clearly augite which has been converted into hornblende. The balance of evidence, consequently, inclined again to a separation of these minerals into two distinct species.

The chemical characters were very imperfectly known. Heinrich Rose had found the non-aluminous augites to be simple bisilicates, $RSiO_3$, and therefore analogous in composition to the magnesia silicate hypersthene, whose cleavage is different, and to the lime silicate wollastonite whose angles are not those of augite. The non-aluminous hornblendes seemed from Bonsdorff's analyses to have a different composition, the oxygen ratio of acid to base being more than 2 : 1; they might be regarded as mixtures of the bisilicate $RSiO_3$ with trisilicate $R_2Si_3O_8$, but if so the relative proportions were not constant. Rammelsberg himself was inclined to believe the mineral to be an isomorphous mixture of these two silicates—rather an advanced view of isomorphism for that date. As for the aluminous augites and hornblendes, they were in hopeless confusion.

It was in 1851 that Rammelsberg seriously grappled with this problem of the augite-hornblende group which had confronted him when he drew up his mineral system in 1847. In the first edition of the "Mineralchemie" in 1875, he was able to incorporate no less than 15 analyses of augites and 15 analyses of hornblendes, made by himself. He had already pointed out that some hornblende undoubtedly has the composition of augite, and some augite undoubtedly has the composition of hornblende. He set himself to discover in particular

whether these minerals do not contain alkalis, whether the iron is ferrous or ferric, and to determine the exact proportions of magnesia and alumina which were at that time only separable with considerable difficulty. Not content with isolated analyses, he undertook a complete revision of the whole group. With the help of Gustav Rose and Krantz, the mineral dealer, he provided himself with the very best material of all the available species; he measured the crystals, revised and recalculated the results of previous observers, and made careful analyses and determinations of the specific gravities, no less than 21 analyses of augites and 24 of hornblendes being recorded.

From the crystallographic point of view, he showed that the lime silicate wollastonite, the soda silicate ægirine, the lime iron silicate babingtonite, and the manganese silicate rhodonite all belong to the same group.

From the chemical point of view, the minerals fall into four groups:

A, containing neither Al nor Fe'''.

B, containing Fe''', but not Al.

C, containing both Fe''' and Al.

D, containing Al, but not Fe'''.

Group A contains many augites, and also the light-coloured hornblendes known as tremolite and actinolite.

Pure tremolite is $CaSiO_3 + 3MgSiO_3$.

Pure diopside is $CaSiO_3 + MgSiO_3$.

Group B contains the following:

Augites.	*Hornblendes.*
Acmite.	Arfvedsonite.
Ægirine	
Babingtonite.	

These are mixtures of $R''SiO_3$ with $Fe_2(SiO_3)_3$ in varying proportions. Hence $Fe_2(SiO_3)_3$ is isomorphous with $R''SiO_3$, and therefore also group B is isomorphous with group A. This was a new conception, and, being reluctant at that time to accept Gerhardt's view concerning the two modifications of iron, Rammelsberg was inclined to regard the relation as due to the dimorphism of the oxide, for Fe_2O_3 is found both in a cubic and a hexagonal form among minerals.

Group C.—Here the investigation involved great labour; special care was required for the separation of aluminium, and the minerals were examined for alkalis and for fluorine. After the analysis of specimens from 15 localities, it was concluded that the aluminiferous augites and hornblendes all contain both FeO and Fe_2O_3, and that all the aluminiferous hornblendes contain K and Na. In previous analyses, the iron had all been reckoned as FeO. It might be

objected that there is no guarantee of the purity of these black, opaque minerals, but Rammelsberg insists that his specimens, although black, are transparent, and are shown by the microscope to be homogeneous. In order to ascertain whether the alumina belongs to the electropositive or the electronegative constituents, he calculated in all the analyses the oxygen ratio for

(1) $RO + R_2O_3 : SiO_2$.

(2) $RO : R_2O_3 + SiO_2$.

(3) $RO + Fe_2O_3 : SiO_2 + Al_2O_3$,

and finding the last alone to be constant and to have the same value for the augites and hornblendes in group C, concluded (1) that augite and hornblende are shown by groups A and B to have the same composition; they must therefore have the same composition in C; and hence (2) Al is an acid and Fe a basic constituent, and the augites and hornblendes are all to be regarded as bisilicates and bialuminates.

Group D contains only spodumene, a lithium sodium aluminium bisilicate in which the aluminium is basic.

In a subsequent paper (1867), Rammelsberg gives up this interpretation and regards the alumina in both the augite and hornblende group as an accessory constituent, Al_2O_3, entering into isomorphous mixture with $RSiO_3$. This idea may be traced to Bonsdorff; it was supposed to be justified by the isomorphism of hæmatite, Fe_2O_3, with ilmenite, $FeTiO_3$.

The subsequent history of these minerals may be added, since it serves to illustrate two features of Rammelsberg's character, his readiness during most of his long career to accept any view which appeared really better than his own, and the conservatism which only overtook him in old age.

In 1871, Tschermak offered an explanation of the aluminiferous augites which was almost universally accepted; their analyses were fully expressed by the formula $mR_2Si_2O_6 + nRAl_2SiO_6$. Subsequently Scharizer offered an explanation of the aluminiferous hornblendes according to which they are mixtures of the mineral actinolite, $CaMg_3(SiO_3)_4$, with a known variety of hornblende having the constitution of a garnet, $R_3Al_2(SiO_4)_3$, to which he gives the name syntagmite. Since the latter can be expressed as $3RSiO_3,Al_2O_3$, it is evident that all such mixtures will agree with Rammelsberg's second hypothesis.

In the second edition of his handbook (1875), Rammelsberg adheres to his old view, but in the Ergänzungsheft (1886) he confesses that Al_2O_3 can hardly be regarded as isomorphous with $RSiO_3$, since Al_2O_3 never has the form of augite, and accepts a more general form of Scharizer's interpretation according to which both augites and hornblendes are isomorphous mixtures of the molecules $RSiO_3$ and

$R_3Al(SiO_4)_3$, and laboriously calculates the various atomic ratios of 56 analyses on this hypothesis.

It is curious that in the second supplement, published in his 83rd year, he should return to his original view and regard Al_2O_3 as isomorphous with $RSiO_3$.

At the present time, Tschermak's explanation is generally made the basis of any speculations upon the constitution of these minerals, but it must never be forgotten that the necessary facts were supplied by Rammelsberg's analyses and by his discovery that they contain both Fe″ and Fe‴.

In any case, whatever explanation be offered, the augite-hornblende group is one of those in which we are driven to accept the intermixture of two molecules having very different constitutions—quite as different as those suggested in other cases by Hermann, whose views are supposed to be long buried and forgotten.

Felspars.—Another example in which such intermixture is perfectly well proved, and even universally accepted, is afforded by the felspar group. The minerals known as albite, oligoclase, labradorite, and anorthite had long been classed together as felspar in spite of differences in composition, but their chemical relations were never understood until Tschermak in 1864 showed that they are not well defined minerals, but pass into each other and that the whole series consists of isomorphous mixtures in varying proportions of the soda-felspar, albite, with the lime-felspar, anorthite. But Rammelsberg had already (in 1850) expressed his conviction that the felspars are an isomorphous group, in spite of the prevalent view that they were distinct minerals. "One and the same type of geometrical form," he says, "scarcely differing more than is usual in isomorphous substances, and a great similarity in all their physical properties unite these minerals which we call in general felspar, and it was only the chemist who found it necessary to separate them because he found that the different members, orthoclase and albite, oligoclase, labradorite and anorthite, cannot be treated as isomorphous by replacement of their individual constituents, but possess compositions which are stochiometrically different, the equivalents of the silica varying in the proportion 12 : 9 : 6 : 4. . . . The observation made upon tourmaline that silicates of different basicity united in different proportions are isomorphous, that is to say, have the same, or nearly the same, form, seems to be repeated in the most important and wide-spread minerals, felspar and mica."

When Tschermak proposed his theory, Rammelsberg, in spite of the opposition of Streng, vom Rath, and others, was the first to give it his warm and undivided support, and here he found a powerful ally in Bunsen. Every subsequent attack upon the theory has only resulted

in its confirmation by renewed analyses, so that at the present time there are no isomorphous mixtures which have been so fully studied, both chemically and physically, and so well established, as those of albite, $NaAlSi_3O_8$, and anorthite, $CaAl_2Si_2O_8$.

The reason why Rammelsberg was so quick to accept the felspar theory of Tschermak and so reluctant to accept his augite theory is easy to see. In the one case, the two constituents were known to exist, in the other case one of them was hypothetical, and no man was more averse to speculation than Rammelsberg.

In 1872, he published a paper entitled "The Present State of our Knowledge of the Felspars," in which he made an elaborate calculation of all the felspar analyses in order to ascertain how closely they agree with Tschermak's formula. This was followed in 1884 by a paper on "Isomorphous Minerals which are not Chemically Analogous," in which, after mentioning olivine, garnet, tourmaline, epidote, and idocrase as minerals whose constituents are analogous, the author admits that silicon, like molybdenum, tungsten, vanadium, &c., forms acids of different basicity; among these, he prefers to accept only the simpler as independent, and regards the more complex as mixtures of these, for example, $H_6Mo_7O_{24}$ as $2H_2Mo_2O_7 + H_2Mo_3O_{10}$. Thus the only silicic acids of which it is necessary to assume the existence are $H_2Si_2O_5$; H_2SiO_3; H_4SiO_4; H_6SiO_5; and H_8SiO_6.

If a salt contains metals of different valencies, it is to be regarded as a mixture of molecules of the same basicity; thus

$$\text{Anorthite, } CaAl_2Si_2O_8 \text{ is } Ca_2SiO_4 + Al_4(SiO_4)_3.$$
$$\text{Albite } NaAlSi_3O_8 \text{ is } Na_4Si_3O_8 + Al_4(Si_3O_8)_3.$$

But we are driven to regard the salts of H_4SiO_4 as capable of entering into isomorphous mixture with the salts of $H_4Si_3O_8$.

Whatever speculations have subsequently been entertained regarding the felspars and other silicates, I fear we must confess that mineral chemistry has not progressed much beyond this point: it is certain that the anorthic soda-lime-felspars are mixtures of albite and anorthite; it is equally certain that no explanation why they should form isomorphous mixtures is sufficiently complete to supply the clue to all the other complex silicates found in Nature.

Towards the end of his life, Rammelsberg returned to the subject again; one of his last papers, published in 1896, contains a number of fresh calculations made with the object of ascertaining which analyses conform to the theory and which deviate from it.

Other Silicates.—Rammelsberg's memoir of 1884 is really inspired by his work on the minerals known as scapolite, chabazite, and phillipsite, which was published in the same year. Here again he

holds by the principle that we are not justified in assuming a mineral to be a mixture of two or more definite silicates unless we have independent evidence of their existence.

Thus in the scapolite group, according to him, sarcolite is $(R'_4R''_2)_3Al(SiO_4)_3$.

Humboldtilite, Meionite, Wernerite } are $mR'_2SiO_3 + nR'_4SiO_4$.

Marialite is $mR'_2SiO_3 + nR'_2Si_2O_5$.

Tschermak's explanation of these minerals as a mixture of two hypothetical silicates he refuses to accept.

Again, in the chabazite group, after an elaborate criticism of all the analyses which indicates that $R'' : Al_2 = 1 : 1$, he selects the three simplest formulæ:

$$R''Al_2Si_3O_{10} + 5H_2O$$
$$R''Al_2Si_4O_{12} + 6H_2O$$
$$R''Al_2Si_5O_{14} + 7H_2O$$

and shows that all the analyses may be interpreted as mixtures of these three molecules.

Similarly, in the phillipsite group, $R'' : Al_2 = 1 : 1$, and the minerals may be regarded as mixtures of:

$$2R''Al_2Si_3O_{10} + 7H_2O$$
$$2R''Al_2Si_4O_{12} + 9H_2O$$
$$R''Al_2Si_6O_{16} + 6H_2O$$

The theory of Fresenius that the minerals of these two last groups can be represented by $m(R''Al_2Si_2O_8 + 4H_2O) + n(R''Al_2Si_6O_{16} + 6H_2O)$ appears to Rammelsberg a mere speculation, since although one of these silicates has the constitution of desmine the other is hypothetical. His views are best expressed in his own words: "When shall we appreciate the fact that we do not yet know the cause of isomorphism, and that equality of form and analogy of composition do not stand to one another in the relation of cause and effect. Nearly forty years ago, Hermann stated the following law:—in isomorphous compounds which are not analogous in composition, there are always two members at the ends of the series, and from their mixture in varying proportions all the remainder result. This he called Heteromerism and endeavoured to establish his views in numerous papers. By the progress of mineral chemistry, the facts upon which this theory was based have been abundantly discredited, and it has never enjoyed the confidence of chemists because it rests upon hypotheses which cannot be tested by experiment. It was therefore a matter of the greatest scientific importance that Tschermak discovered the law of

mixture in the soda-lime-felspars, and it would be equally important to establish similar laws in other groups in which similarity of form is accompanied by difference in composition. But for this, it is necessary that the terminal members of the series should be really known, and that, as with the felspars, the composition of every mixture should by the atomic ratios of its elements supply a *proof* of the law."

Towards the end of his long life, it was perhaps natural that Rammelsberg should feel himself somewhat out of sympathy with the views of younger chemists. One of the fruitful conceptions in modern mineral chemistry has been that of the mutual replacement of hydroxyl and fluorine which has been brought forward by Penfield and established in the case of several minerals. The first of these was the lithium-aluminium phosphate, amblygonite, in which the proportion of water was found to vary between 1·75 and 6·61, and that of fluorine between 11·26 and 1·75. Penfield showed that in all the analyses $P:Al:R:(F,OH)=1:1:1:1$, so that if the water be calculated as hydroxyl replaceable by fluorine, the formula becomes quite simple. Wagnerite and triploidite were already recognised as isomorphous.

In 1884, Rammelsberg expressed himself as follows on this view: "The hypothetical atomic group hydroxyl, which plays a great part in modern chemistry, is now beginning to figure in the formulæ of minerals. Penfield having found in some amblygonites less fluorine and more water, regards all these as unaltered compounds in which HO replaces fluorine; according to this, potassium fluoride and potash would be analogous compounds. I have already protested against this highly unchemical view."

Penfield has subsequently confirmed his theory by analyses of herderite, hamlinite, topaz, and other minerals; it enabled him to give to topaz the beautifully simple formula $Al_2(F,OH)_2SiO_4$. But even with these before his eyes, Rammelsberg in the second supplement to his "Mineralchemie" (1895) repeats that the theory is "in hohem Grade unchemisch"; he persisted in regarding the water in topaz as merely due to incipient decomposition.

It must be remarked that a very recent research by Fels, published in the present year, has failed to find any replacement of hydroxyl by halogen elements in the benzene derivatives.

Professor Penfield, in writing to me about Rammelsberg as a mineral chemist, uses the following words:

"He was without question a man of great energy and enthusiasm, and he accomplished an enormous amount of work. When I studied Rammelsberg's early tourmaline papers, I was impressed by the magnitude of the undertaking, and with the excellent character of the work. He made at the outset a mistake in deciding that tourmaline had no water, and in assuming that loss

on ignition was SiF_4, and, having once made the mistake, he seemed never to be able to get his analyses into good shape. He revised the analyses from time to time, always changing some of the figures, and no man probably will ever be able to tell just what results Rammelsberg placed most confidence in. He practised a sort of chemical sleight-of-hand work with his results, moulding H_2O and F somewhat to suit his own ideas. I believe that his results, as modified by Foote and me in our paper on tourmaline, and founded on the assumption that the bases were probably determined with a good degree of accuracy, are fairer than any of Rammelsberg's own modifications of his analyses. Although Rammelsberg could be very severe as a critic, he seemed to me to be a man of tender feeling. He took occasion to criticise me at one time, stating that my ideas concerning the composition of amblygonite were *rein unchemisch*. I am willing to admit that following the method adopted by Rammelsberg, and writing the composition of amblygonite $Al_2P_2O_8,2LiF$ with isomorphous $Al_2P_2O_8,2LiOH$ was somewhat *unchemisch*, although I did not intend to convey the idea that amblygonite contained a soluble neutral salt, LiF, and a soluble alkali, LiOH, any more than Rammelsberg intended to convey the idea that apatite contained soluble $CaCl_2$ when he wrote the composition as $3Ca_3P_2O_8,CaCl_2$. It certainly is a decided improvement to write amblygonite $Li(AlF)PO_4$ with isomorphous $Li(Al,OH)PO_4$. On the subject of the isomorphism of fluorine and hydroxyl, he said that he could not bring himself to believe in it. To him, water in topaz, for example, would indicate partial decomposition."

Upon some groups of minerals he held quite peculiar views. The arsenic and antimony compounds of iron, nickel, and cobalt, he regarded as isomorphous mixtures of these elements, in fact as alloys; in one of his last papers (1897), he extends this view to the sulphur which these minerals contain, and explains the whole group either as mixtures R_nA_mS, or as mixtures of this molecule with RS_2. Other instances might be quoted in which his own interpretations of the analyses which he had made have not been generally accepted.

If it was difficult to give a summary of Rammelsberg's work in chemistry on account of the extent of his labours, in mineralogy it is quite impossible; to give a catalogue of the minerals which he analysed would be to mention about two-thirds of the mineral kingdom; they can be extracted from his handbook of mineral chemistry, which contains references to all of them. I have contented myself with mentioning a very few of the more important, and especially such as led to the discussion of general principles. Among those which I have been compelled to pass over are the memoirs on mica, on the borates, the tantalates and niobates, on epidote, idocrase, and a host of other large groups, not to mention tourmaline, which is now the subject of lively discussion between Penfield, Clarke, Tschermak, and others. Rammelsberg published important memoirs on this subject in 1850 and 1870, and returned to it in 1890. I believe that he was engaged upon another memoir on tourmaline at the time of his death.

It is noteworthy that in a science which has suffered terribly from the over-multiplication of names, Rammelsberg was entirely free from this infirmity of intellectual conceit, and probably added fewer mineral names to the literature in proportion to the work which he did than any other mineralogist. In order to emphasise this fact, a list of the new names which he introduced is subjoined :

Antimonial arsenic.	Gotthardite.
Castillite.	Heteromorphite.
Chiviatite.	Hydromagnocalcite.
Chlorapatite.	Magnoferrite.
Crednerite.	Pseudolibethenite.
Cuprodescloizite.	Sigterite.
Epichlorite.	Tachydrite.
Fluorapatite.	Waldheimite.
Ginilsite.	Xonotlite.

Writing to Wolcott Gibbs in 1882, Rammelsberg complains that since the duties of the second professorship at the University had been added to his other occupations he had very little leisure for work ; but his ideas of work and leisure were not those of other men. How, among the numerous investigations to which I have already alluded, he found time for research in other subjects besides mineralogy, is hard to understand. There are yet two other important branches of his work which must not be overlooked. In Humboldt's "Cosmos," he is alluded to as "a sagacious chemist who has recently devoted himself uninterruptedly, and with equal activity and success, to the analysis of aerolites," and numbers of his memoirs relate to the analysis of meteorites. Another considerable group of his published papers contain laborious rock analyses ; and in 1854 he had made for Humboldt an analysis of the trachyte of Chimborazo. A paper published in 1847 dealt with the inorganic materials contained in plants. Before middle life, he had attained the reputation of being the most experienced inorganic chemist in Europe. Among the letters which he received are to be found requests from Brooke, Miller, and Lettsom, in England, that he should analyse minerals which they had discovered ; from Schliemann, in Germany, that he should determine the composition of metals from Ilios ; from Lawrence Smith, in America, that he should introduce certain methods of silicate analysis into Germany ; from Grailich, in Vienna, that he should supply him with crystals of the substances which he had analysed. Many of his papers were translated into other languages as soon as they appeared.

Writing in 1852, James Dana says, "Your researches are to me always the highest authority." And again, in 1876, "Your 'Handbuch' gives me anew an exalted idea of the value of your labours for the

progress of mineralogical science. I have carried forward my studies so much of the time with your book in hand that I feel as if I had always enjoyed your companionship and your personal aid, and I may add that it was this aid which made my work possible."

Senarmont, in 1855, cannot refrain from writing to the author of the "Handbook of Crystallographic Chemistry," although he does not know him personally, to express his appreciation of its great value, and his desire to assist Rammelsberg in these labours, in which, he is sure, Marignac joins him.

Marignac himself, in 1881, referring to the second edition, writes, "You have already rendered chemists a great service in your preceding work by giving them everything relating to the crystalline form of chemical compounds, but the service is still greater now that you have added a description of all the physical properties. This must have involved immense labour, and science will always owe you a debt of thanks."

In addition to his own treatises and memoirs, Rammelsberg published translations of Dumas' "Philosophie der Chimie," of Percy's "Metallurgy," and of several papers, such as that of Berzelius on mineral classification, and of Scacchi on polysymmetry.

It would be inconceivable that one man could accomplish all the work which I have now surveyed without assistance, even in a long lifetime, and many of the mineral analyses which issued from Rammelsberg's laboratory were made wholly or in part by his assistants. I find in his treatise on mineral chemistry the names of more than 60 assistants or pupils mentioned as responsible for the analysis of as many minerals; his own analyses are, of course, far more numerous. This will serve to indicate the activity of his laboratory and at the same time, perhaps, the fact that his heart was always really more in the development of research than in the routine work of education; in fact, I do not think that he ever undertook much of the personal supervision of the laboratory during the later part of his career.

I have quoted Professor Liveing's recollection of Rammelsberg as he was in the early prime of life. Dr. Liebert, who worked with him towards the end of his career as a teacher, tells me that the name of Rammelsberg always recalls to his mind the vision of a little man, with his head thrust half into the balance case, rapidly changing the weights with a quick, nervous action. All such operations he conducted with extraordinary rapidity. He was never without a cigar held in the corner of his mouth, and always encouraged his students to smoke in the laboratory. At that time he was still engaged in analytical work, although his hand shook so much that he used a silver wash-bottle for fear of breakage. Dr. Liebert says that he was

extraordinarily accurate in his lectures, and very rarely showed that absent-mindedness (Zerstreutheit) which is a proverbial failing of German professors; he recalls only one occasion on which Rammelsberg lost his equilibrium. "He was lecturing on the oxygen compounds of nitrogen. As usual, the demonstrator had prepared the different experiments beforehand. All went well until nitric oxide was reached; the Professor had stated that vividly burning bodies undergo further combustion when brought into contact with this gas, and proceeded to illustrate this by experiment. Having first introduced several heated metal wires which burnt with a vivid light, and having repeated the experiment with potassium and burning phosphorus, he finally asked for sulphur, which he ignited and introduced into the gas. The flame was quickly extinguished. Rather irritated, he repeated the experiment—with the same result! Rammelsberg prided himself on his accuracy, and began to grow vexed at the repeated failure. With an angry glance at the demonstrator he demanded flowers of sulphur. The result was the same. This was too much for Rammelsberg's patience; turning abruptly to the demonstrator, he said in an 'undertone' distinctly audible to all, 'You have made a mistake; this carelessness will not do,' and turning to his audience, apologised for the mistake which his demonstrator had made in preparing the wrong gas.

"When the demonstrator repeated the process after the lecture, and compared what he had done with the notes of Rammelsberg's handbook, he found the explanation of 'his' mistake. The statement in the notes was:—vividly burning bodies undergo further combustion in NO (examples enumerated); burning sulphur is extinguished."

Among the many chemists or mineralogists who at different times worked with him are to be mentioned Liveing, Wolcott Gibbs, Groth, Max Bauer, Rüdorff, Friedheim, Stahlschmidt, Philipp, and Schöne.

As a lecturer and teacher he was, according to the testimony of all his pupils, admirably lucid and thorough; but what seems to have impressed them most was his indomitable energy in research; he would spare no trouble in repeating the experiments of others; he would spend weeks, or even months, in ascertaining by practical experience the best methods before entering on a difficult analysis; he was supremely careful in obtaining the best possible mineral specimens for analysis; many of them he must have been obliged to purchase for himself at a considerable cost. Mineral chemistry has suffered much in the past from the fact that early analyses were made upon indifferent material, and that there is usually no evidence to show exactly what was used for analysis. Rammelsberg's analyses have never been doubted, his material was beyond reproach, and it is

satisfactory to know that the original specimens which he employed are now in the Berlin Museum fur Naturkunde; I have little doubt that any further research which may ever be done upon these specimens will only tend to confirm the accuracy of his work, which was maintained until he became too old to carry out analysis at all. Even the very last of his published analyses, those of tourmaline, are quoted with high approval by Penfield, and were regarded by Rammelsberg himself as among his very best.

His labours met with full recognition abroad, and he was an honorary member of more than thirty scientific societies.

It only remains to mention the simple events of his life subsequent to the point at which it was left above, namely, the year 1874, when he was made ordinary Professor of inorganic chemistry in the University of Berlin. In 1859, he had married his second wife, the daughter of the well-known naturalist, Chr. G. Ehrenberg; by her he had two sons and one daughter, all of whom survive him. In 1883, he ceased to be Professor at the Gewerbe-akademie (which was transferred as the Technische Hochschule to Charlottenburg), and was made Director of the newly-founded second chemical institute of the University. There was much discussion concerning this appointment, to which Kopp might possibly have been elected, but it was felt that the director of a teaching laboratory ought to be pre-eminently a practical analyst, and no one had higher qualifications in this respect than Rammelsberg.

All his subsequent work was carried on in this laboratory, where his mineral analyses were continued uninterruptedly for nine years.

In 1891, owing to failing eyesight, he retired from all the appointments which he held, and resided quietly for the remainder of his life at Gross Lichterfelde, in the neighbourhood of Berlin, in a house which he had built adjoining that of his married daughter.

In 1892, he underwent an operation which restored his vision, and he was able to devote himself for the next seven years to the recalculation of mineral formulæ and the writing of the second supplement to his "Mineralchemie;" in this he was aided by the care of his loving wife, to whom he dictated much of his latest work. The evening of the old man's life was a happy and peaceful close to an honourable and active career; his ambitions were realised; his family was settled in life; his faculties were unimpaired. Even now, although he was troubled by frequent headache, the veteran chemist was never idle, but when lying on the couch in his library would call his wife from the next room and dictate to her the thoughts which entered his mind.

Professor Penfield, one of the leading representatives of the modern school, has told me of a visit which he paid to Rammelsberg in his

old age, when he had begun to feel himself out of touch with the younger school of mineral chemists. It was an interesting occasion for both, and to my mind it marks a chapter in the history of mineralogy: the termination of the old rigid reading of isomorphism and the introduction of wider views concerning replacement which are destined to simplify the interpretation of mineral analyses. Professor Penfield writes: "It was in the summer of 1894 that I saw him, when he was 81 years old. He was living a very quiet life at Gross Lichterfelde, near Berlin, and his home seemed to be an ideal one for an elderly man. He was at that time still engaged in scientific work, although he was not strong enough to do very much. He presented me, for example, with a copy of one of his recent articles, in which he criticised my views concerning the chemical composition of staurolite, and he showed me the manuscript for the completion of his "Mineralchemie," which was printed one or two years later. I especially enjoyed hearing him tell of Berzelius, the Roses, and men of that generation, for he knew them well and appreciated their qualities. . . . He said that it was a keen pleasure for him to differ from others; it added a certain spice and zest to life to have and hold scientific opinions at variance to those of others. He certainly was a most friendly and genial old gentleman."

It is pleasant to think of the old man softened in character but still retaining the fierce love of battle and adhering doggedly to his views.

Those who knew him towards the close of his life were most impressed by his extraordinary juvenility; he possessed a power of work, a keenness of debate, and a freshness of memory which few retain at such advanced years. His power of concentration enabled him to work undisturbed and rapidly among any distractions. Even when he was an old man, the presence of his little grandchildren was no hindrance to him while writing.

His interest was throughout his life so centred in his scientific work that he had few relaxations, and did not take much interest in general literature; books of travel were his chief delight. He possessed an extraordinarily retentive memory, and astonished his friends by his knowledge of the facts of history and geography; his acquaintance with modern languages was extensive.

In early life he travelled a good deal during his vacations, but always made the best use of his time for scientific purposes, studying the geology of the countries in which he stayed, and collecting minerals for analysis. One of his early journeys was to Sweden (1844), and for the purpose of visiting Berzelius; another (1867) was a geological tour in Auvergne, in company with the well-known mineralogist,

Professor Sadebeck; he was twice sent to Paris (1855 and 1867) by the Government to act as a representative at international exhibitions. Only in later life were his journeys made as pleasure trips.

His keenness of memory and juvenility of mind remained to the end of his life, and he found great pleasure in recounting reminiscences of his travels and of the men whom he had known. Writing to Wolcott Gibbs in 1893, he says, "I have left my 80th year behind, and have for the last two years given up all educational work. Except, however, for the weakness of old age, I feel myself to be active both in mind and body."

It was not till he had attained the age of 86 that the peaceful and industrious evening of his life was brought to a close. He had never completely recovered from an attack of influenza which had prostrated him a few years previously; in the winter of 1899 he was thrown back by an attack of bronchial catarrh, and on the 28th of December sank to final rest from his labours after a life of unexampled industry.

His character recalls irresistibly the spirit of Browning's grammarian:

> "He knew the signal and stepped on with pride
> Over men's pity,
> Left play for work and grappled with the world
> Bent on escaping.
> 'What's in the scroll,' quoth he, 'thou keepest furled?'"

The great men of genius when they die leave the example of a life which all can admire but to which few can attain; the men of great talent, like Rammelsberg, who make unceasing use of their powers, and by a life of industry contribute, perhaps, equally to the increase of knowledge, leave an equally valuable legacy, an example that all can emulate.

I.—2 : 3 : 5-*Trichlorobenzoic Acid.*

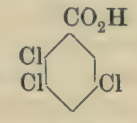
By Francis Edward Matthews.

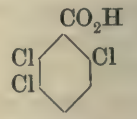
In a paper on the hexachlorides of benzonitrile, benzamide, and benzoic acid, it was stated that alcoholic soda acted on the nitrile in two stages, the first being the removal of three molecular proportions of hydrogen chloride, with the production of trichlorobenzonitrile, and the second the hydrolysis of the cyano-group, with the formation of a mixture of sodium trichlorobenzoates. On repeating this work on a larger scale, it was found that, by the continued fractional crystallisa-

tion of the barium salts of the mixed acids, a new trichlorobenzoic acid could be isolated in a state of purity.

The process had to be carried out on a considerable scale to obtain a satisfactory result, and the yield of the pure acid left much to be desired. Shortly afterwards, it was found that by the action of quinoline on the nitrile, the nitrile of the same trichlorobenzoic acid could be obtained almost quantitatively, and this proving to be readily volatile with steam, was easily purified.

Of the six theoretically possible trichlorobenzoic acids, four have already been obtained, the missing ones being:

I. 

II. 

As the acid obtained from the nitrile did not agree in its properties with any of those previously described, the new acid must have one of the formulæ given above. It was therefore thought worth while to subject it to a complete investigation, with a view of determining its constitution, and also of preparing derivatives by which it could afterwards be readily identified.

Early in the research, the position of the chlorine atoms relatively to one another was readily shown to be 1:2:4, but as both formulæ conform in this respect, the position of the carboxyl group was still uncertain, and many attempts were made to determine its position by preparing nitro- and other derivatives of the acid, but no definite evidence was thereby obtained. The position of the carboxyl group was finally fixed by a process of elimination. In formula II, both ortho-positions relatively to the carboxyl group are replaced by chlorine, and as Victor Meyer and his pupils have shown in similar cases, the acid thus constituted should not be capable of esterification by the action of hydrogen chloride and alcohol. As the new acid is found to yield an ester readily under these conditions, it follows that formula II is inadmissible, and that the substance is 2:3:5-trichlorobenzoic acid.

Experimental.

Benzonitrile Hexachloride and Alcoholic Soda.

Benzonitrile hexachloride was warmed with excess of alcoholic sodium hydroxide. The alkali first removes three molecular proportions of hydrogen chloride, the hydrolysis of the cyano-group taking place subsequently when the solution is boiled. On completion of the reaction, and when no further evolution of ammonia was observed, the mixture was treated with excess of hydrochloric acid, and the precipi-

tated acids, after thorough washing, were converted into the barium salts by boiling with water and excess of barium carbonate.

On fractional crystallisation, the barium compound was found to be a mixture, and, with some difficulty, a nearly pure barium salt was obtained, which gave the following figures on analysis:

0·3140 gave 0·0269 H_2O and 0·1144 $BaSO_4$. $H_2O = 8·56$; $Ba = 21·42$.
$C_{14}H_4O_4Cl_6Ba,3H_2O$ requires $H_2O = 8·44$; $Ba = 21·42$ per cent.

The acid obtained from this salt melted at 156°. It was afterwards found that neither it nor the barium salt was quite pure, and as a much better process for the preparation of the acid was found, the decomposition of the nitrile by means of sodium hydroxide was abandoned.

Benzonitrile Hexachloride and Quinoline. Preparation of 2:3:5-*Trichlorobenzonitrile.*

The removal of three molecular proportions of hydrogen chloride from benzonitrile hexachloride can be more conveniently effected by interaction with quinoline than with sodium hydroxide, and as the trichlorobenzonitrile is volatile with steam, it is easily obtained in a pure condition. The method by which the preparation was carried out is as follows.

Ten grams of benzonitrile hexachloride are placed in a 30—40 oz. fractionating flask, and treated with quinoline in slight excess. No reaction takes place in the cold, but on warming, the nitrile dissolves, and decomposition occurs, indicated by the change in colour of the solution. The reaction, once started, proceeds without any further application of heat, although towards the close it may be advisable to heat slightly in order to complete it. The solid mixture, when cool, is treated with slight excess of dilute sulphuric acid and subjected to distillation with steam, the almost colourless solid trichlorobenzonitrile distilling over readily. After recrystallisation from alcohol, the trichlorobenzonitrile was analysed, with the following result:

0·1026 gave 0·2141 AgCl. $Cl = 51·62$
$C_7H_5NCl_3$ requires $Cl = 51·57$ per cent.

2:3:5-*Trichlorobenzonitrile* crystallises from aqueous alcohol (50—60 per cent.) in beautiful, long, white, lustrous needles which melt sharply at 87°. It has a most nauseating odour, is readily volatile with the vapour of water or alcohol, dissolves easily in all the ordinary organic solvents, and is readily hydrolysed by alcoholic alkali hydroxides, forming a salt of the corresponding benzoic acid.

2:3:5-*Trichlorobenzoic acid.*

The acid can be obtained by precipitation of a solution of the potassium or sodium salt with a mineral acid, and may be purified either by recrystallisation from water or by conversion into the barium salt. It crystallises from hot water in small, colourless needles. In cold water, it is practically insoluble. It melts at 163° without decomposition. It is very soluble in most ordinary organic solvents, but large crystals have not been obtained from any solution. It does not volatilise with steam. On analysis, the following figures were obtained:

0·3464 gave 0·6606 AgCl. Cl = 47·18.
0·2436 „ 0·4642 AgCl. Cl = 47·14.
$C_7H_3O_2Cl_3$ requires Cl = 47·23 per cent.

In order to determine the position of the chlorine atoms, an attempt was made to remove carbon dioxide from the acid by means of caustic baryta. On heating together 2 grams of the pure acid with excess of baryta, a very violent reaction resulted in the loss of all the material employed. A more successful result was attained in the following manner. Two grams of acid were heated in a sealed tube with sulphuric acid (75 per cent.) for 2½ hours at 300°. On opening the tube there was a considerable pressure of gas and a good deal of charring had taken place, but on the surface of the almost black sulphuric acid a nearly colourless layer of oil was floating. This was extracted with ether and the ether distilled off, an oil being left which had the odour of trichlorobenzene and remained liquid on standing. To prove its constitution, it was nitrated and the solid nitro-compound obtained, after purification, melted at 58—59°. The oil, therefore, was 1:2:4-trichlorobenzene, and the position of the chlorine atoms, relatively to one another in the original acid, was thus fixed.

The *barium* salt, $(C_6H_2Cl_3{\cdot}CO_2)_2Ba,3H_2O$, is readily prepared in the pure state by boiling together in water a mixture of the acid and excess of barium carbonate until no further action takes place. On filtering off the excess of barium carbonate and concentrating the solution, the barium salt crystallises out in very characteristic lustrous thin plates. The appearance of the crystals is much altered by the presence of even very small quantities of other substances. The salt is readily soluble in hot water but only sparingly so in cold, being much less soluble than the corresponding strontium and calcium salts; it is therefore the best salt to select for purifying the acid. On analysis:

0·4245 gave 0·0353 H_2O and 0·1547 $BaSO_4$. H_2O = 8·32; Ba = 21·58.
$C_{14}H_4O_4Cl_6Ba,3H_2O$ requires H_2O = 8·44; Ba = 21·42 per cent.

The *strontium* salt, $(C_6H_2Cl_3{\cdot}CO_2)_2Sr,3H_2O$, is prepared similarly

to the barium salt. It crystallises in fine colourless prisms. On analysis:

0·4351 gave 0·0401 H_2O and 0·1339 $SrSO_4$. $H_2O = 9·22$; $Sr = 14·68$.
$C_{14}H_4O_4Cl_6Sr,3H_2O$ requires $H_2O = 9·15$; $Sr = 14·82$ per cent.

The *calcium* salt, $(C_6H_2Cl_3·CO_2)_2Ca,4H_2O$, prepared similarly to the barium salt, crystallises from water in beautiful, lustrous needles. On analysis:

0·1831 gave 0·0234 H_2O and 0·0439 $CaSO_4$. $H_2O = 12·78$; $Ca = 7·05$.
$C_{14}H_4O_4Cl_6Ca,4H_2O$ requires $H_2O = 12·65$; $Ca = 7·13$ per cent.

The *silver* salt, $C_6H_2Cl_3·CO_2Ag$, is prepared by the double decomposition of a hot solution of any of the above salts with silver nitrate, and crystallises in rosettes of needles. It is anhydrous and almost insoluble in cold water, but dissolves slightly on heating. On analysis:

0·2199 gave 0·0940 AgCl. $Ag = 32·17$.
$C_7H_2O_2Cl_3Ag$ requires $Ag = 32·50$ per cent.

The low result is due to the difficulty of completely decomposing the salt with hot strong hydrochloric acid. The salt is not sufficiently soluble in hot water to obtain a solution from which the silver can be precipitated.

The *chloride*, $C_6H_2Cl_3·COCl$, was obtained by the action of excess of phosphorus pentachloride on the acid. After the action ceased, the mixture was thrown into cold water, when an oil separated which very soon solidified; this was dried and then dissolved in hot benzene. On evaporation, an oil was again left which crystallised when cold, and melted at 36°. This was again crystallised by spontaneous evaporation from a solution in ethyl acetate and the crystals thus obtained also melted at 36°. On analysis:

0·1440 gave 0·3380 AgCl. $Cl = 58·06$.
$C_7H_2OCl_4$ requires $Cl = 58·19$ per cent.

The *amide*, $C_6H_2Cl_3·CO·NH_2$, prepared by the action of ammonium carbonate on the acid chloride, crystallised from hot dilute acetic acid in small needles melting at 204—205°.

The same substance has also been obtained by the action of quinoline upon the hexachloride of benzamide. This reaction does not yield a single product, as the amide obtained has to be recrystallised several times before the melting point above mentioned is reached. The purified amide from this source was hydrolysed, and the acid thus obtained was compared, by means of its salts, with the acid prepared from tri-

chlorobenzonitrile, when the identity of the two was established. On analysis:

0·1037 gave 0·1973 AgCl. Cl = 47·07.
$C_7H_4ONCl_3$ requires Cl = 47·43 per cent.

Trichloronitrobenzoic Acid, $NO_2 \cdot C_6HCl_3 \cdot CO_2H$.

Trichlorobenzoic acid is readily nitrated. The acid dissolves at once in fuming nitric acid on warming. On allowing the mixture to stand at a temperature of about 60° for some hours and then diluting with water, a yellowish oil separates which soon crystallises. This acid, on recrystallisation from alcohol, melts sharply at 158°. The fact that it is a mononitro-acid was ascertained by the preparation and analysis of its barium salt. Some of the acid was boiled with hot water, under which it fused, and excess of barium carbonate was added; the acid dissolved gradually and, after filtration and evaporation, a *barium* salt was obtained which crystallised in yellowish, flat needles having a silky lustre. On analysis:

0·3322 gave 0·0423 H_2O and 0·0980 $BaSO_4$. H_2O = 12·73; Ba = 17·35.
0·5522 ,, 0·0657 H_2O. H_2O = 11·89.
$C_{14}H_2O_8N_2Cl_6Ba,5H_2O$ requires H_2O = 11·75; Ba = 17·8 per cent.

The want of sharpness in these figures is probably caused by the presence of a small amount of the barium salt of a dinitro-acid.

On losing its water of crystallisation, the substance becomes bright yellow in colour.

Many unsuccessful attempts were made to remove carbon dioxide from the acid and from the barium salt in order to obtain the corresponding trichloronitrobenzene, and thus throw light upon the constitution of both the trichlorobenzoic acid and its nitro-derivative. Heating with lime or baryta gave too vigorous a reaction, and decomposition in a sealed tube at 250—300° with 75 per cent. sulphuric acid gave chiefly tarry substances, although in one experiment a very small amount of a crystalline substance was isolated. It could not be identified, however, as the present literature of the trichloronitrobenzenes is far from complete.

A *dinitro*-acid is also produced by the action of a mixture of strong sulphuric and nitric acids on the mononitro-acid. It gave a barium salt which crystallised from water in canary-yellow, nodular masses. As no definite evidence as to constitution was obtained by its means, it was not further investigated.

Attempts were also made to reduce the mononitro-acid to the corresponding amino-derivative. With sodium amalgam, an acid was ob-

tained which crystallised from alcohol in colourless needles, melted sharply at 228°, and gave a bright grass-green copper salt on precipitating its solution with cupric acetate.

As, however, in the meantime, definite evidence of the constitution of the trichlorobenzoic acid was obtained by another method, the investigation of these compounds was not carried further.

Ethyl Trichlorobenzoate.—Since the trichlorobenzoic acid must have one of the formulæ previously mentioned, an attempt was made to esterify it by means of hydrogen chloride and alcohol. Two grams of the pure acid were dissolved in absolute alcohol and the mixture was saturated with hydrogen chloride and allowed to stand overnight. On the addition of water, an oil was precipitated which smelt like ethyl benzoate, but less powerfully; this was washed with sodium carbonate solution and water and thoroughly dried but after standing for one month did not crystallise. It volatilised with steam fairly readily, but after purification in this way still remained liquid. On analysis:

0·2132 gave 0·3611 AgCl. Cl = 41·90.

$C_9H_7O_2Cl_3$ requires Cl = 42·01 per cent.

This result agrees well with that required for ethyl trichlorobenzoate, and on this evidence the constitution of the trichlorobenzoic acid ($CO_2H : Cl_3 = 1 : 2 : 3 : 5$) is considered to be proved.

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II.—*The Nitration of Benzeneazosalicylic Acid.*

By J. T. Hewitt and J. J. Fox.

Although nitro-derivatives of benzeneazosalicylic acid have already been described, the compounds have been produced by coupling a diazotised nitraniline with salicylic acid, and hence contained the nitro-group in the benzene nucleus. By this process, Meldola (Trans., 1885, **47**, 666) obtained *p*-nitrobenzeneazosalicylic acid, and Gebek the corresponding meta-derivative (*Annalen*, 1888, **251**, 188). Isomeric compounds containing a nitro-group in the salicylic acid residue have not hitherto been described, although from the results obtained on submitting benzeneazophenol to the action of warm dilute nitric acid (Trans., 1900, **77**, 99) it appeared very probable that a benzeneazo-*o*-nitrosalicylic acid should be formed by a similar nitration of benzeneazosalicylic acid. As a matter of fact, benzeneazosalicylic acid furnishes

a nitro-derivative different from any of the nitrobenzeneazosalicylic acids, and the compound produced was found to be identical with a synthetical benzeneazonitrosalicylic acid, in which the nitro-group stood in the ortho-position relatively to the hydroxyl group. On the other hand, benzeneazosalicylic acid nitrated in concentrated sulphuric acid solution furnished *p*-nitrobenzeneazosalicylic acid, the reaction therefore being quite analogous to that observed by Noelting (*Ber.*, 1887, **20**, 2997) in the case of benzeneazophenol. This observation furnishes an indirect proof that even the azosalicylic acids are converted into quinonehydrazones by strong acids, although no salts with such acids have been isolated.

Benzeneazo-o-nitrosalicylic Acid, $C_6H_5\cdot N{:}N-C_6H_2(CO_2H)(OH)(NO_2)$.

Ten grams of benzeneazosalicylic acid were made into a paste with 45 c.c. of water and 20 c.c. of nitric acid (sp. gr. 1·36), and warmed gently to 65—70°. The thermometer suddenly rose to about 85°, nitrous fumes were evolved, and a reddish, pasty mass resulted. This was quickly poured into water, cooled, and the flocculent precipitate collected and washed free from nitric acid with cold water. The substance, after drying, was usually found to weigh 5½ to 6 grams, and to melt between 160° and 170°. After two recrystallisations from dilute alcohol, a substance melting constantly at 197° * was obtained.

The substance separates in clusters of small, yellowish-red needles; it is easily soluble in alcohol, acetone, or glacial acetic acid, whilst it is also fairly easily soluble in boiling water. The solubility in hydrocarbon solvents is, however, slight. On analysis, results were obtained showing that the substance, crystallised from dilute alcohol and air dried, contains one molecular proportion of water of crystallisation.

0·8456 lost 0·0498 on drying at 110°. $H_2O = 5·88$.
0·1100 gave 13·2 c.c. moist nitrogen at 19° and 756 mm. $N = 13·72$.
$C_{13}H_9O_5N_3,H_2O$ requires $H_2O = 5·90$; $N = 13·80$ per cent.

The dried substance was also analysed:

0·0807 gave 0·1619 CO_2 and 0·0225 H_2O. $C = 54·72$; $H = 3·12$.
0·1112 „ 15·5 c.c. moist nitrogen at 23° and 746 mm. $N = 15·31$.
$C_{13}H_9O_5N_3$ requires $C = 54·32$; $H = 3·16$; $N = 14·66$ per cent.

In order to determine the constitution of the substance, various unsuccessful attempts were made to remove the carboxyl group. It was thought that prolonged heating with acetic anhydride might effect the

* This melting point as well as the others given in this paper are not corrected for the apparent coefficient of expansion of mercury.

elimination of carbon dioxide, whilst the hydroxyl group would be acetylated at the same time. Instead of this, the carboxyl group was found to be very firmly attached, and this and the nitro-group being both in ortho-positions relatively to the hydroxyl, protected the latter from acetylation. Heating in a reflux apparatus with benzoyl chloride led to the production of tarry substances, from which no crystalline matter could be isolated. The process of heating the barium salt with an excess of caustic baryta was also a failure, explosion regularly occurring as soon as a temperature of 155° was reached.

The substance had of necessity to be compared with a synthetical product obtained by coupling phenyldiazonium chloride with an alkaline solution of nitrosalicylic acid, [$CO_2H : OH : NO_2 = 1 : 2 : 3$]. The latter compound was obtained by nitration of salicylic acid in an acetic acid solution, and separated from the 1 : 2 : 5-isomeride by Hübner's method (*Annalen*, 1879, **195**, 6), which depends on the sparing solubility of the barium salt of the 1 : 2 : 3-compound. The purity of the nitrosalicylic acid was checked by the melting point.

In coupling the nitrosalicylic acid with diazonium compounds, the same difficulty is experienced as in the case of *o*-nitrophenol, reaction taking place slowly and incompletely. Since the diazonium salt yields decomposition products difficult of removal, it is as well to use the nitrosalicylic acid in slight excess. The process consists in adding a well-cooled solution of phenyldiazonium chloride to an alkaline solution of nitrosalicylic acid, and allowing the interaction to proceed for three days in a cool place ; the solution is then filtered from deposited matter and acidified. The precipitate contains the desired azo-compound mixed with a considerable excess of nitrosalicylic acid. To effect a separation, the mixed acids are dissolved in hot dilute ammonia solution and ammonium and barium chlorides added. Barium *o*-nitrosalicylate, although easily soluble in boiling water, is very sparingly soluble in the cold, whilst the barium salt of the azo-acid dissolves very slightly even in boiling water. The precipitate obtained consists essentially, therefore, of barium benzeneazo-*o*-nitrosalicylate, and if the acid is liberated from the salt and the process of purification by means of the barium salts repeated, it is obtained in such a condition that when mixed with the product of direct nitration no depression of melting point is observed.

In addition to this direct proof of the constitution of the azo-acid, it may be mentioned that by reduction of an alkaline solution with hydrogen sulphide, aniline as one of the fission products may be detected with the greatest certainty by the ordinary reactions (volatility with steam, isonitrile reaction, bleaching powder test, and production of tribromoaniline). We have been unable to isolate the

diaminosalicylic acid, which must form the other fission product, on account of its ready oxidisability.

Benzeneazo-*o*-nitrosalicylic acid dissolves in concentrated sulphuric acid with a far yellower shade than benzeneazosalicylic acid; possibly the nitro- and carboxyl groups in the ortho-position relatively to the hydroxyl exert a sufficient attraction on the hydrogen of the hydroxyl to prevent isomerisation of the compound to the quinone-hydrazone form. This subject will, it is hoped, be further examined; if it were found that nitration in concentrated sulphuric acid solution led to the production of *p*-nitrobenzeneazo-*o*-nitrosalicylic acid, it would at least be rendered probable that isomerisation had taken place.

A solution of the acid in ammonia or fixed alkalis is red in colour. The ammonium salt was found to furnish the following precipitates:

Silver Nitrate.—Concentrated solutions give an orange precipitate somewhat soluble in water and easily soluble in ammonia.

Lead Acetate.—Yellowish-red precipitate insoluble in hot water.

Mercuric Chloride.—A yellow precipitate, somewhat soluble in a large quantity of water.

Stannous Chloride.—A yellow precipitate even in dilute solutions. This dissolves on warming, and does not appear to come down again on cooling. Excess of sodium hydroxide gives a deep red solution turned to a light red shade by excess of dilute hydrochloric acid.

Ferrous Sulphate.—A chocolate-coloured precipitate, turning greenish-brown on warming. The liquid becomes at the same time deep red.

Ferric Chloride.—A dark red solution and precipitate.

Cobalt Nitrate.—A yellow precipitate soluble in hot water.

Nickel Sulphate.—A dirty yellow precipitate soluble in hot water.

Magnesium Chloride.—An orange precipitate slightly soluble in hot water.

Barium and Calcium Chlorides.—Orange precipitates, soluble in a large quantity of boiling water.

Dyeing experiments were also made. Wool mordanted with iron gives a rich brown, with alumina a bright yellow, and with potassium dichromate, a dull yellow shade.

The *methyl ester* was prepared from 2 grams of the acid, 10—12 grams of methyl alcohol, and 1 c.c. of sulphuric acid. The mixture was warmed in a reflux apparatus for 5 hours, poured into water after the greater portion of the alcohol had been distilled off, and the precipitate collected, washed, and recrystallised from spirit. The substance forms small, brown needles melting at 132—134°.

0·0827 gave 0·1675 CO_2 and 0·0294 H_2O. C = 55·23 ; H = 3·95.
0·1080 „ 12·6 c.c. moist nitrogen at 18° and 760 mm. N = 13·48.
0·1094 „ 13·2 c.c. „ „ 18° „ 759 mm. N = 13·92.
$C_{14}H_{11}O_5N_3$ requires C = 55·77 ; H = 3·68 ; N = 13·96 per cent.

The *ethyl ester* was prepared in a similar manner from the acid, sulphuric acid, and 95 per cent. ethyl alcohol. It forms very small, yellow needles melting at 128—129°.

0·1290 gave 14·7 c.c. moist nitrogen at 22° and 760 mm. N = 12·91.
$C_{15}H_{13}O_5N_3$ requires N = 13·33 per cent.

p-*Nitrobenzeneazosalicylic acid* has already been described by Meldola (Trans., 1885, **47**, 666). It may be obtained by gradually adding 2·1 grams of powdered potassium nitrate, in small portions at a time, to a solution of 5 grams of benzeneazosalicylic acid in 100 c.c. of concentrated sulphuric acid. Care should be taken that the temperature does not rise above 20° during the operation ; the mixture is then allowed to stand in the cold for 48 hours, after which it is poured into a large volume of water, collected, washed free from acid, and dried. The substance is already practically pure and the yield nearly theoretical. On recrystallisation, it was obtained as brilliant red needles. Meldola states that the melting point of the substance cannot be observed on account of blackening taking place above 225°. Our specimen, as well as one obtained from diazotised *p*-nitraniline and salicylic acid, did not blacken until a considerably higher temperature was reached, and by immersing the melting point tubes in sulphuric acid previously heated to 245—250°, both specimens were observed to melt at 253—254° (uncorr.), decomposition and blackening then taking place. The two preparations when mixed showed no depression of melting point. On analysis :

0·1124 gave 14·7 c.c. moist nitrogen at 16° and 750 mm. N = 15·04.
$C_{13}H_9O_5N_3$ requires N = 14·66 per cent.

The *ethyl ester* of this acid was prepared from both specimens in the usual manner. Each preparation melted at 220—225°, a certain amount of decomposition taking place.

0·1165 gave 14·3 c.c. moist nitrogen at 23° and 759 mm. N = 13·82.
$C_{15}H_{13}O_5N_3$ requires N = 13·33 per cent.

Both the *m*- and *p*-nitrobenzeneazosalicylic acids resist the action of dilute nitric acid to a greater degree than the unsubstituted acid. Attempts at nitration, even at 100°, led to the recovery of nearly the whole of the original acids in an unchanged condition.

East London Technical College.

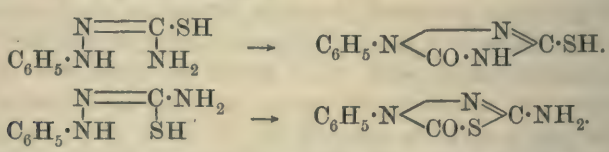
III.—*Oxidation of Benzalthiosemicarbazone.*

By George Young, Ph.D., and William Eyre, B.Sc.

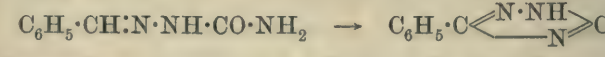
It has been shown by Marckwald (*Ber.*, 1892, **25**, 3098; 1899, **32**, 1081) that certain thiosemicarbazides, for example,

$$C_6H_5\cdot NH\cdot N{:}C(SH)\cdot NH_2,$$

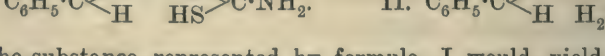
exist in two forms, of which the labile modification when treated with phosgene yields a mercaptotriazole, whilst the stable form with the same reagent yields an aminothiodiazolone. This difference, Marckwald ascribes to stereoisomerism, thus:



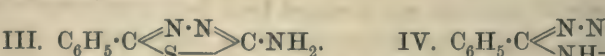
Young and Witham having found that benzalsemicarbazone could be oxidised by ferric chloride to phenylhydroxytriazole (Trans., 1900, **77**, 224),



we thought it might be of interest to apply the same reaction to benzalthiosemicarbazone in order to determine, if possible, whether this compound would act as a mixture, or as one or the other of the two possible stereoisomeric forms:



The substance represented by formula I would yield an aminophenylthiodiazole, III, whilst that represented by II would yield a phenylmercaptotriazole, IV.

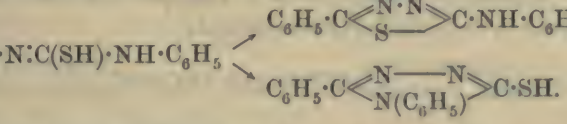


The oxidation of benzalthiosemicarbazone by ferric chloride takes place much more easily than that of benzalsemicarbazone; the latter requires to be heated with an alcoholic solution of ferric chloride in sealed tubes at 130—140°, whereas the thio-compound is oxidised by aqueous ferric chloride between 70° and 80°. The product consists almost entirely of the hydrochloride of a base which has the properties to be expected of an aminothiodiazole. In one or two experiments, there was also obtained a trace of a substance of high melting point and soluble in alkali, which may have been the mer-

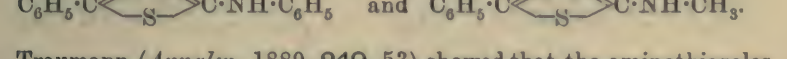
captotriazole, but the quantity obtained was too small to admit of purification. Benzalthiosemicarbazone reacts, therefore, with ferric chloride almost, if not entirely, as if it had the constitution represented by formula I. Changes in the conditions under which the oxidation took place produced no effect on the nature of the product.

We endeavoured, but without success, to obtain a second form of benzalthiosemicarbazone.

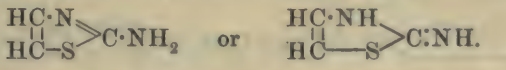
Our results being negative do not preclude the possibility of a second form, but, on the other hand, the substance may be tautomeric, and might, with another oxidising agent, yield the mercaptotriazole in the same manner as, according to Marckwald and Bott (*Ber.*, 1896, **29**, 2914), benzoyl-4-phenylthiosemicarbazide yields phenylamino-phenylthiodiazole when treated with acetyl chloride, but diphenylmercaptotriazole when acted on by excess of benzoyl chloride, or when heated above its melting point,

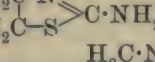
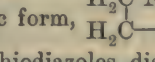


Benzal-4-phenylthiosemicarbazone and benzal-4-methylthiosemicarbazone undergo oxidation by ferric chloride to the corresponding phenylamino- and methylamino-phenylthiodiazole :



Traumann (*Annalen*, 1889, **249**, 53) showed that the aminothiazoles can be equally well represented as iminothiazolines :



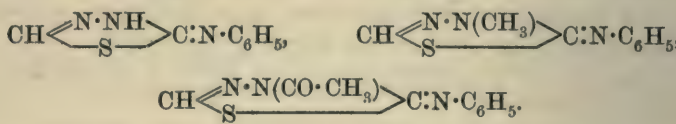
Gabriel (*Ber.*, 1889, **22**, 1144 ; 1898, **31**, 2832) found the aminothiazolines,  , to react sometimes as such, sometimes as the tautomeric form,  .

The aminothiodiazoles discussed in this paper are very similar in structure to the above compounds, and although we make use, as far as possible, of the "amino" nomenclature and constitutional formulæ, the reactions and properties of our substances might be represented just as well by the "imino" constitution.

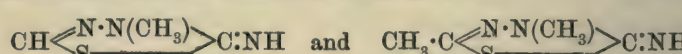
The structure of the methyl and acetyl derivatives of aminophenylthiodiazole is of some interest in connection with the work of Pulvermacher and of Freund on the aminothiodiazoles.

Pulvermacher (*Ber.*, 1894, **27**, 613) found that phenylaminothiodi-

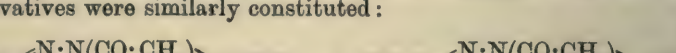
azole on methylation and subsequent decomposition yielded aniline and methylamine, and he therefore gave to the base, the methyl derivative, and the acetyl derivative the respective formulæ:



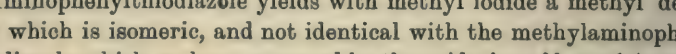
Freund and Meinecke (*Ber.*, 1896, **29**, 2511) methylated aminothiodiazole and aminomethylthiodiazole, and by comparison with the corresponding synthetical bases prepared by Pulvermacher, determined the constitution of the methyl derivatives to be



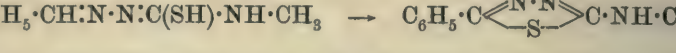
and, following Pulvermacher's example, assumed that the acetyl derivatives were similarly constituted:



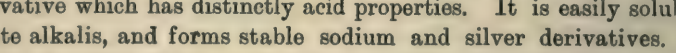
Aminophenylthiodiazole yields with methyl iodide a methyl derivative which is isomeric, and not identical with the methylaminophenylthiodiazole which we have prepared by the oxidation of benzal-4-methylthiosemicarbazone:



To the methyl base prepared by methylation and to its acetyl derivative, we must ascribe the constitutional formulæ:

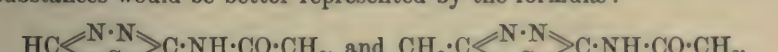


Aminophenylthiodiazole yields with acetic anhydride an acetyl derivative which has distinctly acid properties. It is easily soluble in dilute alkalis, and forms stable sodium and silver derivatives. The action of methyl iodide on the silver acetyl compound yields a methyl acetyl derivative which is identical with the above acetyl derivative of the methylated aminophenylthiodiazole. The acetyl derivative of aminophenylthiodiazole must therefore have the constitution

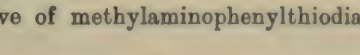


We consider that there is no ground for the assumption that the methyl and acetyl groups take up the same position when an aminothiodiazole is methylated or acetylated, and as our acetylaminophenylthiodiazole closely resembles the acetyl derivatives described by Freund

and Meinecke, we are of opinion that the constitution which they ascribe to these acetyl compounds is open to doubt, and that their substances would be better represented by the formulæ:



The acetyl derivative of methylaminophenylthiodiazole has probably the constitution:



Experimental.

Benzalthiosemicarbazone, $C_6H_5\cdot CH{:}N\cdot N{:}C(SH)\cdot NH_2$.—Thiosemicarbazide, prepared according to the method described by Freund and Imgart (*Ber.*, 1895, **28**, 948), was dissolved in warm alcohol and benzaldehyde added. On cooling, part of the benzalthiosemicarbazone crystallised out in hair-like needles, and the remainder was precipitated by the addition of water.

Benzalthiosemicarbazone is easily soluble in warm alcohol, and slightly so in boiling water, from which it crystallised, on cooling, in long, thin, shining plates which melted at 156°. After recrystallisation from alcohol, the substance melted at 159—160°.

Benzalthiosemicarbazone has slightly acid properties, as it is fairly soluble in caustic soda, and is reprecipitated by dilute hydrochloric acid.

0·2140 gave 0·2716 $BaSO_4$. S = 17·41.

$C_8H_9N_3S$ requires S = 17·87 per cent.

Benzalthiosemicarbazone is easily oxidised by aqueous ferric chloride. The oxidation commences at about 70°. The best results were obtained by suspending the benzalthiosemicarbazone in water, adding rather more than one molecular proportion of ferric chloride, and warming for half an hour in a water-bath at 80—90°. After filtering from a small amount of solid matter A, the filtrate was slightly concentrated, if necessary, and and allowed to cool.

The hydrochloride of the oxidation product crystallised out in white needles which, after recrystallisation, melted at 213—214°. Further quantities of less pure hydrochloride were obtained by concentrating the mother liquors.

The hydrochloride contains one molecular proportion of water of crystallisation, which is given off at 90°.

0·2904 gave 0·1810 AgCl. HCl = 15·86.

0·5172, at 90°, lost 0·0420 H_2O. H_2O = 8·12.

0·3312, dried at 90°, gave 0·2182 AgCl. HCl = 16·76.

$C_8H_7N_3S,HCl,H_2O$ requires HCl = 15·76; H_2O = 7·77 per cent.

$C_8H_7N_3S,HCl$ requires HCl = 17·10 per cent.

The solid matter, A, consisted principally of unchanged benzalthiosemicarbazone, but in some experiments contained also a very small amount of a substance of higher melting point which was soluble in alkalis. This substance, which was not further investigated, may have been the mercaptotriazole isomeric with the base which formed the chief product.

Aminophenylthiodiazole, $C_6H_5 \cdot C\begin{matrix}<\\ S\end{matrix}\!\!\begin{matrix}N \cdot N\\ -\end{matrix}\!\!>C \cdot NH_2$.—The hydrochloride obtained by the oxidation of benzalthiosemicarbazone was dissolved in water and excess of ammonia added. The precipitated base on recrystallisation from 50 per cent. alcohol, formed colourless, microscopic hexagonal plates which melted at 222—223°.

0·2148 gave 0·4294 CO_2 and 0·0800 H_2O. C = 54·52; H = 4·14.
0·2570 ,, 55 c.c. moist nitrogen at 23° and 755·2 mm. N = 23·96.
0·2456 ,, 0·3194 $BaSO_4$. S = 17·83.
$C_8H_7N_3S$ requires C = 54·24; H = 3·95; N = 23·72; S = 18·08 per cent.

The base is easily soluble in dilute acids. On addition of concentrated hydrochloric acid to the solution in dilute acid, the hydrochloride described above is obtained.

Acetylaminophenylthiodiazole, $C_6H_5 \cdot C\begin{matrix}<\\ S\end{matrix}\!\!\begin{matrix}N \cdot N\\ -\end{matrix}\!\!>C \cdot NH \cdot CO \cdot CH_3$.—The base was added to an equal weight of acetic anhydride. The mixture rapidly became hot and soon solidified. The product on recrystallisation from boiling alcohol formed small needles which melted at 276°.

0·3052 gave 0·3214 $BaSO_4$. S = 14·44.
$C_{10}H_9ON_3S$ requires S = 14·61 per cent.

The acetyl compound is very slightly soluble in water, moderately so in boiling alcohol, and easily so in aqueous alkalis. A sodium derivative is precipitated by the addition of concentrated aqueous caustic soda to the solution in the dilute alkali.

The silver derivative was prepared by dissolving the acetyl compound in dilute ammonia and running the solution into aqueous silver nitrate. The white precipitate was washed with water and alcohol.

0·1742 gave 0·0576 Ag. Ag = 33·07.
$C_{10}H_8ON_3SAg$ requires Ag = 33·13 per cent.

Acetyliminomethylphenylthiodiazoline,

$$C_6H_5 \cdot C\begin{matrix}<\\ S\end{matrix}\!\!\begin{matrix}N \cdot N(CH_3)\\ -\end{matrix}\!\!>C{:}N \cdot CO \cdot CH_3.$$

—The silver acetyl derivative was treated with methyl iodide and methyl alcohol, and after standing overnight was heated for half an

hour at 100° in a sealed tube. The product, recrystallised from boiling alcohol, formed prismatic needles melting at 144°.

0·2378 gave 37·7 c.c. moist nitrogen at 14° and 751·2 mm. N = 18·43.
0·2578 „ 0·2534 $BaSO_4$. S = 13·48.
$C_{11}H_{11}ON_3S$ requires N = 18·03 ; S = 13·73 per cent.

Iminomethylphenylthiodiazoline, $C_6H_5\cdot C\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}N\cdot N(CH_3)\\ S\end{matrix}>C{:}NH$.—Aminophenylthiodiazole was heated with methyl iodide and methyl alcohol in a sealed tube for 1 hour at 100°. On cooling, the hydriodide of the new base crystallised out in large, flat prisms which melted at 245—246°. On addition of aqueous caustic potash to the hydriodide, the base separated as an oil. The hydrochloride melts at 218—219°, and the platinichloride at 217—218°. On analysis of the latter :

0·3134 gave 0·0776 Pt. Pt = 24·76
$(C_9H_9N_3S)_2,H_2PtCl_6$ requires Pt = 24·62 per cent.

On adding the base to acetic anhydride heat was developed and on cooling the acetyl derivative crystallised out. This compound has the same melting point (144°) and crystalline appearance as the acetyliminomethylphenylthiodiazoline described above. It was analysed with the following result :

0·1410 gave 22·4 c.c. moist nitrogen at 16·5° and 744·2 mm. N = 18·08.
$C_{11}H_{11}ON_3S$ requires N = 18·03 per cent.

Benzal-4-methylthiosemicarbazone, $C_6H_5\cdot CH{:}N\cdot N{:}C(SH)\cdot NH\cdot CH_3$, was prepared according to Pulvermacher's directions (*Ber.*, 1894, **27**, 623) and its properties agreed with his description.

0·1368 gave 26·2 c.c. moist nitrogen at 16° and 740·0 mm. N = 21·72.
$C_9H_9N_3S$ requires N = 21·76 per cent.

This compound was oxidised with ferric chloride in exactly the same way as benzalthiosemicarbazone. The hydrochloride which separated was treated with aqueous caustic potash and the base thus obtained was crystallised from alcohol.

Methylaminophenylthiodiazole, $C_6H_5\cdot C\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}N\cdot N\\ S\end{matrix}>C\cdot NH\cdot CH_3$, is moderately soluble in hot alcohol, from which it separates in shining plates melting at 183—184° ; it is fairly soluble in benzene, from which it crystallises in flat needles, and very slightly soluble in hot water from which it is deposited in microscopic, rough needles.

0·0950 gave 18·3 c.c. moist nitrogen at 15° and 744·2 mm. N = 22·07.
$C_9H_9N_3S$ requires N = 21·99 per cent.

From the hydrochloride a platinichloride was prepared which melted at 208—209°.

0·5526 gave 0·1352 Pt. Pt = 24·46.

$(C_9H_9N_3S)_2,H_2PtCl_6$ requires Pt = 24·62 per cent.

Methylacetylaminophenylthiodiazole, $C_6H_5\cdot C\begin{matrix}N\cdot N\\ S\end{matrix}C\cdot N\begin{matrix}CH_3\\ CO\cdot CH_3\end{matrix}$.—Methylaminothiodiazole was added to an excess of acetic anhydride. The acetyl compound crystallised from alcohol in long needles which melted at 195°.

0·1314 gave 20·6 c.c. moist nitrogen at 15° and 744·2 mm. N = 17·99.

$C_{11}H_{11}ON_3S$ requires N = 18·03 per cent.

Benzal-4-phenylthiosemicarbazone, $C_6H_5\cdot CH{:}N\cdot N{:}C(SH)\cdot NH\cdot C_6H_5$, was made by the action of benzaldehyde on 4-phenylthiosemicarbazide. It melted at 190° and agreed in its properties with those described by Pulvermacher (*loc. cit.*). It was boiled for half an hour with an alcoholic solution of ferric chloride. The product, which separated on dilution and evaporation of the alcohol, was treated with caustic soda. The resulting base, which melted at 199—200°, was easily soluble in boiling alcohol. It formed a hydrochloride insoluble in water but soluble in alcoholic hydrochloric acid. With acetic anhydride, it formed an acetyl derivative melting at 140°. The properties of the base agree fully with Marckwald and Bott's (*loc. cit.*) description of phenylaminophenylthiodiazole, $C_6H_5\cdot C\begin{matrix}N\cdot N\\ S\end{matrix}C\cdot NH\cdot C_6H_5$.

0·3464 gave 3·3266 $BaSO_4$. S = 12·35.

$C_{14}H_{11}N_3S$ requires S = 12·65 per cent.

When an alcoholic solution of the base is poured into alcoholic silver nitrate, a white precipitate is formed. On analysis:

0·6860 gave 0·2070 Ag. Ag = 30·17.

$C_{14}H_{10}N_3SAg$ requires Ag = 30·00 per cent.

This silver derivative when air-dried is stable at the ordinary temperature; when suddenly heated, it decomposes with explosive violence and with the evolution of phenyl*iso*nitrile.

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IV.—*A Simplified Method for the Spectrographic Analysis of Minerals.*

By Walter Noel Hartley, F.R.S. and Hugh Ramage, F.I.C., A.R.C.Sc.I.

Prior to the close of the eighteenth century the composition of minerals was never stated quantitatively, and even now in all cases where the analysis of a mineral is of importance, it is necessary first to know the nature of its constituents before determining their proportions. Testing by the blow-pipe was first systematically employed by J. Gahn, and very extensively applied to mineral analysis by him and by Bergman (Thomson's "Annals of Philosophy," 1818, 40, 40—47. See Thomson's "History of Chemistry," 2, 199, edition of 1831); it was afterwards in many respects perfected by Wollaston and Plattner. Its application is limited when unaided by other methods, thus in minerals of a complex composition it is difficult to detect small quantities of beryllia and some of the other rare earths when associated with alumina and magnesia.

The method of dissolving minerals by the action of special solvents and separating their constituents by the addition of suitable precipitants was first systematised by Klaproth, and largely practised by Vauquelin, who not only improved analytical processes, but reduced the art of analysis to a greater degree of simplicity and precision. The work was advanced to a greater measure of perfection by Berzelius, Heinrich Rose, and many others down to the present day. This is the method *par excellence* both for qualitative and quantitative purposes, but it is tedious when carried out in minute detail, and requires to be applied with considerable judgment, tact, and skill. It is frequently necessary to supplement it by other methods, as for instance in the detection of small quantities of beryllium, yttrium, cæsium, or rubidium. Spectrum analysis of minerals found a pioneer in Swan (*Trans. Roy. Soc. Edin.*, 1853, 20, 335), the inventor of the collimator, and Bunsen, who with Kirchhoff devised the first serviceable spectroscope for the chemist's use, and applied it practically to mineral analysis. It is hardly necessary to refer to the discoveries of gallium, indium, thallium, rubidium, and cæsium. Spectrum analysis is the only absolute method of diagnosing the chemical composition of a mineral, or of a substance separated by precipitation in the course of a chemical analysis. As no two substances can give the same spectrum, it follows that the spectrum of a substance is peculiar to itself, and, provided that light sufficient in amount and in purity can enter the instrument, it is immaterial how far from a self-luminous object the

observer is distant. Moreover, it is possible to determine the composition of materials too minute in quantity to be handled, and which cannot therefore be submitted to chemical analysis. We are also able to determine the composition of a substance the constituents of which are not amenable to any known process of chemical separation. Notwithstanding these advantages, this method in some directions does not completely satisfy the requirements of the chemist.

It is desirable that a marked distinction should be drawn between chemical analysis, spectrum analysis, and merely chemical testing. The first implies the actual separation of the constituents of a substance by taking advantage of their differences in volatility, solubility, or other chemical properties; spectrum analysis is the separation in the order of wave-length of the rays proceeding from any material either self-luminous or not, and the identification of these rays with the presence of a substance whether element or compound to which these rays belong. This physical method when suitably modified in detail can very advantageously be employed as an aid to, and with certain limitations even instead of, chemical analysis.

The Method of Spectrographic Analysis.

Oxyhydrogen flame spectra both of elements and compounds have been closely investigated and described by one of us and shown to be capable of very useful applications (Hartley, *Phil. Trans.*, 1894, **185**, A, 161, 1029). Photographs of spectra are produced with extreme ease either from metals, oxides, or other compounds in the solid or liquid state. The alkali metals were proved to be volatilised from refractory silicates by reason of the high temperature employed. A general application of this fact led to a method of examination being devised whereby the spectra of the alkalis can be separated from those of the alkaline earths even in a Bunsen flame (Hartley, Trans., 1893, **63**, 138). We have also shown by a study of manganese slags and siliceous minerals containing this element that it can be volatilised in the oxyhydrogen flame by simply heating the silicate.

Owing to the high temperature to which the substances are subjected, it has already been shown that platinum wire supports are of no use, and fragments of a highly crystalline silicate of alumina in the form of the mineral kyanite have been substituted (Hartley, "Flame Spectra at High Temperatures," *Phil. Trans.*, 1894, **185**, A, 168).

Later it was found that little rods of pure alumina, also chips off the bowls of clay tobacco pipes, could serve the purpose of supports, and that solutions as well as solid salts, minerals, or metals could conveniently be examined therewith.

We propose now to give an account of a simplification of the method of obtaining these spectra, together with some examples of its application to the chemical analysis of very minute quantities of mineral substances.

If the substance to be examined is a metal it should be in the form of filings, turnings, powder, or metallic sponge. If a mineral, it should be finely powdered. In either case, the powder in quantity up to half a gram is rolled up in one-half of an "ashless" filter paper about 5 inches in diameter, the powder is spread equally over the paper with exception of a strip at the edge, and is kept as near to the centre of the roll as possible, that it may be in the midst of the reducing gases given off by the paper when charred and in contact with the carbon. In this manner at so high a temperature, some oxides which are non-volatile or are volatilised with great difficulty, as they do not undergo dissociation in the flame, are actually reduced and a spectrum of the metal is thus obtained. For example, we find that certain lines in the spectrum of zinc and even that of aluminium may be photographed when the oxides are burnt in this way. As regards the thermochemistry of the substance, this fact is of considerable interest because it informs us of the possibility of reducing aluminium oxide in presence of carbon at the temperature of the oxyhydrogen flame. In the electric arc the product is aluminium carbide. The lines referred to have approximately the wave-lengths 3962 and 3944, and correspond with two of the strongest lines of aluminium common to the arc and spark spectrum, namely, those with wave-lengths 3961·68 and 3944·26 (Kayser and Runge).

In front of the spectrograph is a quartz lens 3 inches in diameter, which projects on to the slit of the instrument the image of the flame from an oxyhydrogen blow-pipe. It is advisable to make the focal length of the lens 4 or 5 inches. That used by us has a focus of 3 inches, and molten particles which adhere to the quartz are liable to be projected on to it, necessitating the repolishing of the lens. The flame may take a vertical or horizontal direction, or a direction inclined towards the optic axis of the instrument. The operator having placed the dark slide containing the sensitive plate in position and exposed it, protects his eyes by wearing very dark neutral tint or black glasses and, seated near the flame, introduces the point of the paper pencil containing the ore or mineral into the lowest part of the flame. As it burns rapidly it is pushed farther in until it becomes necessary to hold the last two or three inches with platinum pointed forceps. Some minerals burn with sparks, others form fused globules which drop off, and care should be taken with these that they do not fall into and choke the oxygen jet of the blow-pipe. One pencil suffices, as a rule, to yield a strong spectrum. The

time occupied in burning is about two minutes, and five spectra can very conveniently be photographed on one plate. A short spark spectrum is generally photographed on the middle of the flame spectrum, by turning the slit of the spectrograph towards the spark emitted by an alloy giving well-known and clearly defined lines, from the measurements of which wave-lengths along the whole spectrum may be deduced by means of a curve. Of course it is advisable first of all to ascertain definitely the substances to be found in the filter papers used; Schleicher and Schüll's ashless filters generally gave weak lines of sodium, and weaker lines of potassium, calcium, and iron. These elements are present in the ash of the filter paper and the dust of the air. Precipitates may be collected on ashless filters and the paper burnt. If the precipitate be small, as, for instance, a few milligrams in weight, the paper is cut into strips and so burnt. The photographs are taken on Edwards' "Snap Shot" isochromatic plates or Cadett's spectrum plates, and are developed with quinol, the development occupying from two to three minutes. When burnt in the manner described, the lines in the spectra are not obscured by the emission of white light, but the presence of a large quantity of sodium salts is decidedly disadvantageous, inasmuch as it overpowers or suppresses weak lines of other elements. The spectra observed for the most part have already been described (*Phil. Trans.*, 1894, **185**, A, 168, 1029). In one or two cases we have considered it advisable to revise these spectra.

The water-vapour lines from the flame, the lines of iron, calcium, and sodium, may be very commonly observed. Precipitates show the spectrum of potassium in a manner which leads to no other conclusion than that this element remains in combination with insoluble hydroxides much more frequently than is generally supposed.

The lines in the spectra are measured directly by applying an ivory scale to the photograph and clamping it to the glass as described elsewhere in the examination of absorption spectra (Hartley, *Phil. Trans.*, 1885, 176, 471).

We have used divided scales 4 inches long with 200 divisions to an inch. A very little practice with a sufficiently powerful magnifier or low-power microscope enables each division to be subdivided by judgment into fifths.

With a curve constructed from the principal lines of iron and either Kayser and Runge's wave-lengths or Rowland's solar lines, we may determine the wave-lengths of any line so accurately that as a rule for the identification of lines of known wave-lengths nothing more is necessary. But occasionally it becomes desirable that wave-lengths be determined with still greater accuracy, and micrometer measurements are resorted to. As an example of what may be accomplished

in this manner, we give in a tabulated statement the lines observed in "blast furnace metal" from Middlesbrough, side by side with the lines with which they have been identified in the solar spectrum or in the arc spectrum of iron. It will be seen that the agreement between the wave-length numbers is very close. We proved the identity of the lines due to foreign metals by carefully executed chemical analyses aided by measurements from the photographs of the spectra of the various precipitated substances which were separated in the process, and not solely from the spectrum of the crude metallic iron.

Lines may be identified in many spectra by simultaneous coincidences with groups of lines on photographed spectra of the elements, without precisely measuring their wave-lengths. In this case, the one plate is placed film to film against the other.

Spectrographic analysis of the crude metal with which the converters are charged at Middlesbrough. The iron was heated in the oxyhydrogen flame on supports of cyanite.

Wave-lengths of lines. (Rowland's scale.)	Lines in solar spectrum for comparison. (Rowland.)	Remarks and references showing by figures the intensity of the lines, (1) being the lowest.
5735·2		Narrow band
5622·2		Edge of band more refrangible.
5582·4		Edge of band more refrangible.
5371·7	5371·686	Fe, Cr (7)
5328·6 {	5328·696	Fe (2)
	5328·747	Fe (2)
5270·2	5270·533	Fe (4)
4481·7	4482·338	Fe
61·5	61·818	Fe (4)
27·3	27·482	Fe (5)
15·7	15·293	Fe (6)
05·1	04·927	Fe (10)
4383·1	4383·720	Fe (15)
75·8	76·107	Fe (6)
25·5	25·939	Fe (8)
07·9	08·081	Fe (6)
4289·9	4289·885	Cr (5)
74·6	74·958	Cr (7 d)
71·5	71·934	Fe (6)
54·4	54·505	Cr (8)
26·8	26·904	Ca (20 d ?)
16·9	15·72	Rb, Rowland, also 4216·351 Fe (3 d ?)
02·4	01·98	Rb, Rowland, also 4202·198 Fe (8)
4171·6	4172·211	Ga (1)
43·6	44·038	Fe (15)
31·4	32·235	Fe (10)
4071·6	4071·908	Fe (15)
63·4	63·755	Fe (20)

Spectrographic analysis, &c. (continued).

Wave-lengths of lines. (Rowland's scale.)	Lines in solar spectrum for comparison. (Rowland.)	Remarks and references showing by figures the intensity of the lines, (1) being the lowest.
4047·4	4047·338	K (1 ?)
45·8	45·975	Fe (20)
44·0	44·294	K (1)
34·5	34·641	Mn (5)
33·2	33·224	Mn (7 d)
31·0	30·914	Mn (7)
05·3	05·408	Fe (7)
3969·1	3969·413	Fe (10)
30·5	30·450	Fe (8)
28·0	28·075	Fe (8)
22·8	23·054	Fe (12 d)
20·0	20·410	Fe (10)
06·4	06·628	Fe (10)
3899·9	3899·850	Fe (8)
95·9	95·803	Fe (7)
86·2	86·421	Fe (15)
78·9	78·720	Fe
72·9	72·639	Fe (6)
65·6	65·674	Fe (7)
60·1	60·055	Fe (20)
56·6	56·524	Fe (8)
49·6	50·118	Fe (10)
40·2	40·580	Fe, C (8)
34·2	34·364	Fe (10)
27·3	27·973	Fe (8)
25·9	26·027	Fe (20)
24·5	24·591	Fe (6)
20·6	20·566	Fe, C (25)
15·6	15·987	Fe (15)
12·6	13·100	Fe (5)
3799·4	3799·693	Fe (7)
98·5	98·662	Fe (7)
94·9	95·147	Fe (8)
87·9	88·046	Fe (9)
67·2	67·341	Fe (8)
63·8	63·945	Fe (10)
58·4	58·379	Fe (15)
49·3	49·631	Fe (20)
48·2	48·408	Fe (10)
45·8	45·717	Fe (8)
37·4	37·231	Fe (30)
35·1	35·014	Fe (40)
33·3	33·469	Fe (7 d ?)
27·9	27·778	Fe (4)
22·5	22·692	Fe (10)
19·9	20·086	Fe (50)
09·3	09·397	Fe (10)
07·9	08·068	Fe (5)
05·7	05·711	Fe (8)
3687·1	3687·607	Fe (8)
83·6	83·202	Fe (6)
79·9	80·064	Fe (8)
47·8	47·995	Fe (10)

Spectrographic analysis, &c. (continued).

Wave-lengths of lines. (Rowland's scale.)	Lines in solar spectrum for comparison. (Rowland.)	Remarks and references showing by figures the intensity of the lines, (1) being the lowest.
3631·2	3631·619	Fe (20)
18·7	18·924	Fe (20)
09·0	09·015	Fe (15)
05·3	05·483	Cr (4)
3593·7	3593·636	Cr (9)
87·6	87·130	Fe (8)
85·5	85·479	Fe (7)
81·5	81·344	Fe (40)
78·8	78·832	Cr (10)
70·1	70·225	Fe (20)
65·5	65·528	Fe (12)
58·6	58·670	Fe (8)
25·9	25·986	Fe (4)
25·0	24·677	Ni (20)
21·2	21·404	Fe (7)
13·7	13·947	Fe (6)
3497·6	3497·991	Fe (7)
90·7	90·721	Fe (10)
76·6	76·831	Fe (8)
75·4	75·594	Fe (10)
71·9	71·499 ?	Fe (3). Identity with 3471·499 doubtful. It is more probably 3472·06 Fe, a reversed line in the arc spectrum (Kayser and Runge).
66·0	65·991	Fe (6)
43·8	44·032	Fe (8)
40·7	40·759	Fe (15)
3301·9	3303·107	Na (5)
01·4	02·501	Na (6)
3273·6	3274·092	Cu (6)
47·0	47·680	Cu (9)

The Spectrographic Analysis of Silicates.

Silicates are sometimes of a very refractory nature and do not yield spectra of the bases present other than the alkalis unless these are in some way liberated and converted either into oxides or salts. A means universally applicable for removing the silica had to be devised. Several methods were tried, but only one which has been in use for thirteen years past in the laboratory of this college appeared in all cases to be satisfactory; that is, to decompose the silicate with a mixture of pure ammonium fluoride and strong sulphuric acid warmed in a platinum crucible which is covered by a lid. It is necessary that the ammonium fluoride and the acid should be pure. To purify the ammonium fluoride from silicon fluoride and from all fixed bases, it is necessary to distil it in a platinum retort, an operation which is not

Examples of the spectrographic analysis of refractory minerals.

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.	Copper.	Silver.	Magnesium oxide.	Calcium oxide.	Strontium oxide.	Aluminium.	Gallium.	Indium.	Thallium.	Iron.	Nickel.	Manganese.	Chromium.	Lead.	Remarks.
(1) Corundum ...		Na	*K*				*Ag*					Ga			Fe					Where the symbol of the element is printed in italics, it means that there were traces only.
(2) Corundum ...		Na	*K*			Cu	*Ag*		*Ca*			Ga			Fe			Cr		
(3) Spinel.....		*Na*	*K*			Cu	*Ag*	MgO				Ga			Fe			Cr		Spinel contains more Cr and Ga than ruby.
(4) Ruby		Na	*K*			Cu	Ag		CaO			Ga			Fe		Mn	Cr		Ruby contains Mn and Cu, and more Fe than spinel.
(5) Rutile.....		Na	K			Cu			CaO						Fe		Mn		Pb	
(6) Basalt.....		Na	K			Cu	*Ag*	MgO	CaO	Sr		Ga			Fe		Mn		Pb	
(7) Serpentine Co. Donegal		Na	K			Cu	Ag	MgO	CaO	Sr					Fe		Mn		Pb	
(8) Hornblende granulite ...		Na	K			Cu	Ag	MgO	CaO	Sr		Ga			Fe	Ni	Mn		Pb	The symbol Ca indicates the calcium line 4226. When the quantity of substance is small this very strong line alone is photographed.
(9) Felsite.....		Na	K	Rb		Cu	Ag		CaO	Sr		Ga			Fe	Ni ?	Mn		Pb	
(10) Felspar (Orthoclase).	Li	Na	K	Rb		Cu			CaO			Ga			Fe		Mn		Pb	The formula CaO shows that the calcium oxide bands in addition are conspicuous.
(11) Muscovite ...		Na	K	Rb		Cu	Ag		CaO		Al	Ga			Fe	Ni	Mn		Pb	MgO indicates bands of magnesium oxide.
(12) Plumose mica	Li	Na	K	Rb	Cs	Cu	Ag		CaO			Ga			Fe	Ni	Mn		Pb	
(13) Lepidolite ...	Li	Na	K	Rb	Cs	Cu			CaO			*Ga*		Tl	Fe		Mn		Pb	
(14) Beryl, Glencullen, Co. Dublin	Li	Na	K	Rb	Cs	Cu	Ag		CaO			Ga		Tl	Fe		Mn		Pb	

(15) Schist containing large garnets		Na	K	Rb		Cu	Ag	MgO	CaO	Sr		Ga		Fe	Ni	Mn		Pb	
Garnets and mica slate, Airolo, Canton Ticino.																			
(16) Garnets		Na	K			Cu	*Ag*	MgO	CaO	Sr		Ga ?		Fe		Mn	Cr	Pb	Gallium doubtful here.
(17) Mica slate ...		Na	K	Rb	Cs	Cu	*Ag*	MgO	CaO	*Sr*	Al	Ga		Fe	Ni	*Mn*		Pb	The mica slate contains also TiO_2 as rutile. Practically all the Mn, Cs, Ga, and Ag crystallise in the mica. The felspar contains a larger proportion of Na, Ca, and Pb, but smaller proportions of Rb and Fe.
Minerals from a coarse granite from Co. Dublin.																			
(18) Felspar	Li	Na	K	Rb	Cs	Cu			CaO		Al	*Ga*		Fe		Mn		Pb	
(19) Mica	Li	Na	K	Rb	Cs	Cu	Ag		CaO			Ga		Fe		Mn		Pb	
(20) Quartz.....		Na	K			Cu			CaO					Fe		Mn		*Pb*	
(21) Clay, Shankhill Quarry, Co. Dublin..	Li	Na	K	Rb	Cs	Cu	Ag		CaO	Sr		Ga		Fe	Ni	Mn	*Cr*	Pb	
(22) Residue, insoluble in HCl, from Cleveland clay ironstone		Na	K	Rb		Cu		MgO	CaO	Sr		Ga		Fe	Ni	Mn	Cr ?	Pb	It is a little doubtful whether chromium is present here.
(23) Shale from ironstone beds		Na	K	Rb ?		Cu	Ag	MgO	CaO	Sr		Ga		Fe	Ni	Mn	Cr	*Pb*	
(24) Bauxite from Wales		*Na*	*K*			Cu	Ag		Ca			Ga		Fe	Ni		Cr		

difficult, since the salt distils freely and does not solidify in the neck of the retort. The purity of the sulphuric acid is of course easily ascertained by ignition in a platinum dish, when it should leave no fixed residue. The proportion of fluoride found convenient will of course differ with the nature and composition of the silicate to be examined. If we take the substance which is perhaps the most refractory, namely, cyanite, because it contains about 96 per cent. of aluminium silicate, we may reckon that for every gram of the mineral there will be required at least two and a half times its weight of ammonium fluoride and five times its weight of oil of vitriol. In practice we find three times its weight of ammonium fluoride and seven times its weight of oil of vitriol are sufficient. These materials may be intimately mixed with the very finely powdered mineral and kept for some time at a temperature of about 50°. When silicon fluoride ceases to be evolved, the temperature may be gradually raised until the sulphuric acid and ammonium sulphate are completely expelled. The solid may be then converted into mixed bases by repeatedly heating with ammonium carbonate and igniting gently.

Lead is found sometimes in ordinary concentrated oil of vitriol by the appearance of one lead line in the spectrum, but when it is desirable to get rid of this impurity, the acid made from sulphur trioxide may be used. The only impurities observed in the spectra, including those yielded by the paper and the sulphuric acid, were traces of sodium, potassium, calcium, and the merest trace of iron.

Otto Vogel has described the use of the oxy-coal gas flame for spectrum analysis, using pieces of retort carbon from gas-works as a support for the substance (*Zeit. anorg. Chem.*, 1894, 5, 42—62). The spectra were not photographed. Such observations were made by one of us using iridium wires as a support as far back as 1885, and the method of examining such minerals as heavy-spar, fluorspar, felspar, and mica in such a flame was taught in the laboratory of the Royal College of Science, Dublin, from that time until 1889 and 1890, when the oxyhydrogen flame and cyanite supports were used.

Silicates such as felspar, mica, &c., we now examine in the following manner. The residue from the treatment of 1 gram with ammonium fluoride, &c., after ignition to expel the ammonium sulphate, is boiled with water and a slight excess of ammonia. The precipitate which contains the alumina, &c., is collected by filtration, dried, and ignited in a roll of filter paper. The residue from the filtrate, after ignition, is collected in a small quantity of water, and the mixture poured on to a filter paper, which is dried and burnt. Two spectra are thus obtained from each mineral, the one of bases precipitable, the other of those which are not precipitable by ammonia. Silicates such as basalt, and those present in siderolites, &c., may contain iron (ferrous or ferric oxide),

calcium oxide, and magnesium oxide, besides the alumina and alkalis. The residue is dissolved in hydrochloric acid, and before precipitating with ammonia the iron must be oxidised. The calcium in the filtrate is prepitated by ammonium carbonate, and the magnesium in the filtrate from this by ammonium phosphate. The filtrate from the magnesium phosphate is then examined as in the preceding case for the alkalis.

The reaction for cæsium and rubidium is more delicate if these bases are first separated from the bulk of the potassium and the sodium by precipitating with platinic chloride and boiling the precipitate with water. Potassium and sodium yield strong continuous spectra which mask weak lines of other elements. Lithium is only detected in the photographed spectra by its blue line and one in the ultra-violet when it is present in appreciable quantity, but traces may be easily detected by eye observation of the red line.

On pp. 68 and 69 a tabulated statement is given of the substances detected by spectrographic analysis in a number of very refractory minerals which were analysed by the method here described.

V.—*The Alkaloid of Hyoscyamus muticus and of Datura Stramonium grown in Egypt.*

By Wyndham R. Dunstan, F.R.S., and Harold Brown, Assistant Chemist in the Scientific Department of the Imperial Institute.

I. *Hyoscyamus muticus.*

In a previous paper (Proc., 1898, **14**, 240; Trans., 1899, **75**, 72), we have shown that the *Hyoscyamus muticus* of India, which has long been used in Indian medical practice, contains the alkaloid hyoscyamine, unaccompanied by other mydriatic alkaloids, so that its isolation in the pure state is a comparatively easy operation.

The percentage of hyoscyamine found by us in the stems and leave of this sample of the Indian plant was 0·1 per cent.

Since the publication of this paper, a short communication has appeared (*Arch. Pharm.*, 1898, **236**, 704) by Dr. Gadamer, in which he states that he has examined *Hyoscyamus muticus* grown in Egypt, and has found in the seed capsules and seeds 1·34 per cent. of hyoscyamine, and in the leaves as much as 1·393 per cent., whilst the stems contained 0·569 per cent. As these quantities are more than ten times as great as those found by us in the Indian plant, we have examined the alkaloid furnished by plants grown in Egypt, which

have been collected for us through the kindness of Mr. E. A. Floyer, Member of the Egyptian Institute.

The plant is very abundant in the desert. The material received weighed about 1·5 kilograms, and consisted of the leaves, stems, and flowers. In many cases, the fruits were fully formed and the seeds ripe. The seed was removed for examination whilst the stems and leaves were operated upon together.

Seeds.—About 60 grams were obtained and thoroughly dried in a current of warm air (about 40°). They were then ground to a fine powder, and the alkaloid extracted by the process previously described (*loc. cit.*). As in the case of the Indian plant, the hyoscyamine was obtained in a crystalline condition. The quantity corresponded with 0·87 per cent., calculated on the dry material. In fractionally crystallising this alkaloid, by adding light petroleum to its solution in dry chloroform, it was nearly all obtained in white, silky needles melting at 105°, which furnished a crystalline aurichloride melting at 160° and containing 31·55 per cent. of gold. There is therefore no doubt that the crystalline alkaloid is pure hyoscyamine. As two very small fractions presented themselves in a gummy, semi-crystalline state, they were converted into aurichloride, and this was fractionally crystallised. Nothing, however, was obtained beyond an aurichloride melting at 160° and containing 31·3 per cent. of gold, so that no other alkaloid than hyoscyamine was present.

Stems and Leaves.—The mixture of stems and leaves was thoroughly dried, finely powdered, and the alkaloid extracted. It amounted to 0·59 per cent. on the dried material. This alkaloid crystallised readily from its solution in chloroform and possessed all the properties of hyoscyamine. A quantity was converted into the aurichloride and fractionally crystallised. All the fractions melted between 159° and 160° and contained between 31 and 31·5 per cent. of gold, so that it may be safely concluded that no other alkaloid than hyoscyamine was present. A non-alkaloidal substance was, however, isolated from the crystalline material first obtained. It was noticed in crystallising the original alkaloid from chloroform. On recrystallising this substance from alcohol, it was obtained in flat, rectangular plates melting at 196—198°. It was not readily dissolved by cold water, although easily soluble when heated; the aqueous solution was quite neutral. It left no residue on ignition, and although it contained nitrogen, did not react with alkaloidal reagents, nor did it exhibit the properties of a base. It was also devoid of acid properties, being only sparingly soluble in cold aqueous alkalis, whilst the solution obtained by heating deposited, on cooling, the unchanged substance. It did not reduce Fehling's solution before or after boiling with dilute sulphuric acid. Its taste was distinctly bitter. The quantity of the substance avail-

able did not allow of its further investigation, but we intend, when a fresh supply of material has been obtained, to investigate its properties more fully.

It thus appears that *Hyoscyamus muticus* grown in Egypt resembles that grown in India in containing practically pure hyoscyamine. The amount of this alkaloid furnished by the Egyptian plant is, however, considerably greater than that yielded by the same plant grown in India. It must, however, be borne in mind that, so far, only one sample of the Indian plant has been examined, and it is well known that the quantity of alkaloid in atropaceous plants varies considerably with their age. The examination of other samples of the Indian plant will, therefore, be necessary before it can be definitely concluded that the larger proportion of alkaloid now found is due to the growth of the plant in Egypt.

The rather larger percentages recorded by Dr. Gadamer may be partly accounted for by his having employed Keller's volumetric method of estimation, whereas we have isolated and weighed the crystalline alkaloid; and partly also by the age of the plant examined, as to which we have no information.

The percentages of hyoscyamine recorded for *Hyoscyamus muticus* grown in Egypt are very much higher than those hitherto recorded for any atropaceous plant, and this, taken with the fact that hyoscyamine can be so readily obtained in a pure condition from this material, makes *Hyoscyamus muticus* a valuable commercial source of this alkaloid.

Mr. Floyer informs us that any quantity can be readily grown in the Egyptian desert, and that a demand for a large supply could easily be met.

II. *Datura Stramonium.*

Through the kindness of Mr. Floyer, we have been enabled to examine a specimen of the *Datura Stramonium* grown in Upper Egypt. The European plant is well known, and somewhat extensively used in medicine. It was at one time supposed to contain an alkaloid daturine, which subsequent research proved to be a mixture of atropine and hyoscyamine. As difference of climate and soil is known to produce considerable alteration in the constituents in plants, we were glad of the opportunity to examine the Egyptian Stramonium.

From the plant as received, consisting of thick, succulent stems, holding large, ripe fruits but very little leaf, the seeds were removed, and the remainder, consisting of the stem, broken leaves, and fruit cases, separately examined.

Seeds.—About 42 grams were obtained and dried in the air. They were then examined in precisely the same manner as those of *Hyos-*

cyamus muticus. 0·35 per cent. of the crystalline alkaloid was obtained melting at 104°, and showing all the characters of hyoscyamine. Its aurichloride, after recrystallisation, melted at 159°, and contained 31·29 per cent. of gold. The whole of the alkaloid was converted into aurichloride, and this was fractionally recrystallised. In no case was any aurichloride obtained other than that of hyoscyamine.

Stems and Leaves.—The mixture of stems and leaves, amounting to about 80 grams, was air-dried and examined in the same manner as *Hyoscyamus muticus*. 0·3 per cent. of alkaloid was obtained, which, however, did not crystallise readily, but separated in a semi-gummy state. The whole of it was therefore converted into aurichloride and fractionally crystallised. With the exception of a minute, granular fraction melting below 130°, which was probably the aurichloride of atropine, the whole of the gold salt was obtained in shiny, crystalline scales characteristic of hyoscyamine aurichloride. They melted at 159°, and contained 31·37 per cent. of gold. The influence of minute quantities of other alkaloids in hindering the crystallisation of hyoscyamine is well known.

It therefore appears that the *Datura Stramonium* of Egypt differs from that grown in Europe in containing hyoscyamine unaccompanied by other atropaceous alkaloids, although, as has been pointed out in the previous paper, the nature of the alkaloid contained in plants belonging to this natural order is liable to vary considerably with age, and therefore this difference may not be in reality a fundamental one.

It is obvious that both these plants merit the attention of those concerned with their utilisation in medicine and pharmacy, as an abundant supply of either could be obtained in Egypt.

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VI.—*The Inversion of the Optically Active* ac-*Tetrahydro-β-naphthylamines prepared by the aid of* d- *and* l-*Bromocamphorsulphonic Acids.*

By William Jackson Pope and Alfred William Harvey.

In order to further investigate the possibilities of the methods devised during recent years for the resolution of externally compensated basic substances (Pope and Peachey, Trans., 1898, **73**, 893; 1899, **75**, 1066, 1127; 1900, **77**, 1072; Pope and Rich, Trans., 1899, **75**, 1093), the

study of Bamberger and Müller's *ac*-tetrahydro-β-naphthylamine (*Ber.*, 1888, 21, 847) was undertaken; this substance, according to the constitution assigned to it by these authors, contains an asymmetric carbon atom.

Resolution of Externally Compensated ac-*Tetrahydro-β-naphthylamine*, $\begin{matrix} CH\cdot CH{:}C\cdot CH_2\cdot CH_2 \\ \| \qquad\qquad | \\ CH\cdot CH{:}C\cdot CH_2\cdot CH\cdot NH_2 \end{matrix}$.

Crude racemic *ac*-tetrahydro-β-naphthylamine hydrochloride is purified by precipitating the carbonate of the base from ether as described by Bamberger and Müller and subsequently evaporating to dryness with hydrochloric acid, or by the simpler but equally efficient method of crystallising it several times from moist boiling acetone; it melts at 242—243° (Noyes and Ballard, *Ber.*, 1894, 27, 1450). In accordance with the method devised by Pope and Rich (*loc. cit.*), hot concentrated aqueous solutions of one molecular proportion of ammonium *d*-bromocamphorsulphonate and of two molecular proportions of racemic tetrahydro-β-naphthylamine hydrochloride are mixed. An immediate separation of the least soluble salt possible in the system takes place in accordance with the equation:

$$d\text{-B,HCl} + l\text{-B,HCl} + NH_3, d\text{-A} = NH_4Cl + l\text{-B,HCl} + d\text{-B},d\text{-A},$$

and, by the time that the solution has cooled to the ordinary temperature, a practically quantitative separation of the *d*-tetrahydro-β-naphthylamine *d*-bromocamphorsulphonate as a mass of colourless needles has been effected. After filtering and washing with cold water, the salt is crystallised from boiling spirit and then from hot absolute alcohol, ethyl acetate being added to the latter solution before cooling.

It may be remarked that this resolution partakes more of the nature of a separation by precipitation than of a separation by fractional crystallisation.

d-ac-*Tetrahydro-β-naphthylamine* d-*Bromocamphorsulphonate*, $C_{10}H_{11}\cdot NH_2, C_{10}H_{14}BrO\cdot SO_3H$.

The salt crystallises in long, colourless needles melting with decomposition at 185—188°, and a solution of 0·4471 gram made up to 25·1 c.c. with absolute alcohol gave α_D +3·08 at 12° in a 200 mm. tube; whence the specific rotatory power $[\alpha]_D$ +86·5. It is very soluble in hot alcohol, but less so in ethyl acetate and very sparingly soluble in boiling water. The following analytical results were obtained:

0·1642 gave 0·3146 CO_2 and 0·0949 H_2O. C = 52·25 ; H = 6·42.
0·1719 „ 0·3285 CO_2 „ 0·0989 H_2O. C = 52·12 ; H = 6·39.
0·4006 „ 0·1679 AgBr. Br = 17·86.
$C_{20}H_{28}O_4NBrS$ requires C = 52·40 ; H = 6·11 ; Br = 17·47 per cent.

Ammonium l-*Bromocamphorsulphonate*.—The *l*-camphor required for the preparation of the hitherto unknown *l*-bromocamphorsulphonic acid is conveniently obtained by treating Schimmel and Co.'s *l*-borneol with successive quantities of nitric acid of sp. gr. 1·42 until no further evolution of red fumes takes place; the product is then poured into water and the precipitated camphor collected, well washed with cold water, and dried. The *l*-camphor thus obtained is brominated by Armstrong and Matthews' method (*Chem. News*, 1878, **37**, 4), and after crystallisation from boiling spirit, *l*-*a*-bromocamphor is obtained in long, colourless needles melting at 76° (compare Haller, *Compt. rend.*, 1887, **105**, 66). The rotatory power was determined in benzene solution, and compared with that of the enantiomorphously related *d*-*a*-bromocamphor, with the following results :

0·4195 gram of *d*-bromocamphor, made up to 25·0 c.c. with benzene, gave α_D +3·93° at 19° in a 200 mm. tube: whence $[\alpha]_D$ +117·1°.
0·4172 gram of *l*-bromocamphor, made up to 25·1 c.c. with benzene, gave α_D −3·93° at 19° in a 200 mm. tube : whence $[\alpha]_D$ −118·2°.

The *l*-bromocamphor, on sulphonation and subsequent treatment by Kipping and Pope's method (Trans., 1895, **67**, 356), yields ammonium *l*-bromocamphorsulphonate having properties similar to those of its stereoisomeride, as is shown by the following determinations of rotatory power :

0·4531 gram of ammonium *d*-bromocamphorsulphonate, made up to 25 c.c. with water, gave α_D +3·06° in a 200 mm. tube at 18·5°: whence $[\alpha]_D$ +84·4° and $[M]_D$ +277°.
0·4559 gram of ammonium *l*-bromocamphorsulphonate, made up to 25·1 c.c. with water, gave α_D −3·06° in a 200 mm. tube at 18·5°: whence $[\alpha]_D$ −84·2° and $[M]_D$ −276°.

The description of derivatives of lævo- and of externally compensated bromocamphorsulphonic acids will form the subject of a future paper.

l-ac-*Tetrahydro-β-naphthylamine* l-*Bromocamphorsulphonate*, $C_{10}H_{11}\cdot NH_2, C_{10}H_{14}BrO\cdot SO_3H$.

The mother liquors remaining after separation of the *d*-bromocamphorsulphonate of the *d*-base are treated with a trifle more than the requisite amount of soda to liberate the base, which is then exhaus-

tively extracted with ether; after washing the ethereal solution with water, the base is precipitated as carbonate, and the latter, dissolved in just the requisite amount of hydrochloric acid, is then treated with a hot aqueous solution of one equivalent of ammonium *l*-bromocamphorsulphonate. A crystalline precipitate of *l*-tetrahydro-β-naphthylamine *l*-bromocamphorsulphonate at once falls, and is purified in the same way as its enantiomorphously related isomeride.

The salt crystallises in colourless needles melting at 185—188° with decomposition, and, after drying at 100°, was analysed with the following results:

0·1527 gave 0·2922 CO_2 and 0·0891 H_2O. C = 52·19; H = 6·48.
0·1668 „ 0·3206 CO_2 „ 0·0965 H_2O. C = 52·42; H = 6·43.
0·4219 „ 0·1747 AgBr. Br = 17·65.
$C_{20}H_{28}O_4NBrS$ requires C = 52·40; H = 6·11; Br = 17·47 per cent.

A solution of 0·4206 gram, made up to 25·1 c.c. with absolute alcohol, gave α_D −2·89° at 16° in a 200 mm. tube: whence $[\alpha]_D$ −86·2°, a result numerically identical with that obtained for the antipodal isomeride.

It may be remarked that, by the successive application to an externally compensated base of the enantiomorphously related *d*- and *l*-bromocamphorsulphonic acids, the practically quantitative resolution of the inactive base into its optically active components becomes possible.

d-ac-*Tetrahydro-β-naphthylamine Hydrochloride*, $C_{10}H_{11}\cdot NH_2,HCl$.

On suspending *d*-tetrahydro-β-naphthylamine *d*-bromocamphorsulphonate, having the specific rotatory power $[\alpha]_D$ +86·5°, in a little water, adding rather more than sufficient soda to liberate the base, extracting with ether, washing the ethereal solution with water, and distilling off the ether after addition of hydrochloric acid, a crystalline residue of the hydrochloride is obtained. This salt, however, proves to be a mixture of the dextro- and racemic hydrochlorides; on crystallisation from hot water, a deposit of salt was obtained which melted at 239—241°, and had a specific rotatory power of $[\alpha]_D$ +32·9° in a 2 per cent. aqueous solution, corresponding to a molecular rotatory power of $[M]_D$ +59°, which, as shown later, is an impossibly low value for *d*-tetrahydro-β-naphthylamine hydrochloride. Further, on dealing with a large quantity of carefully purified *d*-bromocamphorsulphonate and systematically crystallising the mixture of hydrochlorides from water and dilute acetone, a specimen of the pure racemic hydrochloride was isolated which melted at 242—243°, did not depress the melting point of an undoubted sample of the salt, and

was optically inactive. The racemic salt was isolated as the most sparingly soluble component of the mixture, and from the mother liquors, pure *d*-tetrahydro-β-naphthylamine hydrochloride was separated as the most soluble constituent by repeated crystallisation. *d*-Tetrahydro-β-naphthylamine hydrochloride crystallises from boiling moist acetone in colourless needles melting at 243—245° and separates in long, flattened needles of glassy lustre during the spontaneous evaporation of its cold aqueous solution. It is practically insoluble in dry organic solvents, but readily dissolves in water. The following analytical results were obtained with the salt dried at 100°:

0·1426 gave 0·3415 CO_2 and 0·1007 H_2O. C = 65·31 ; H = 7·85.
0·1308 ,, 0·3136 CO_2 ,, 0·0916 H_2O. C = 65·39 ; H = 7·78.
0·2160 ,, 0·1699 AgCl. Cl = 19·46.
$C_{10}H_{14}NCl$ requires C = 65·43 ; H = 7·63 ; Cl = 19·30 per cent.

A solution of 0·3645 gram, made up to 25·2 c.c. with water, gave α_D +2·08° at 12° in a 200 mm. tube; whence $[\alpha]_D$ +71·9° and $[M]_D$ +131·9°.

In moist acetone solution, the salt has about twice as high a rotatory power as in water; since, however, the values vary with the amount of moisture present in the acetone, they need not be quoted.

l-ac-*Tetrahydro-β-naphthylamine Hydrochloride*, $C_{10}H_{11}\cdot NH_2,HCl$.

In just the same way, it was found that optical inversion takes place during the preparation of *l*-tetrahydro-β-naphthylamine hydrochloride from its *l*-bromocamphorsulphonate ; the racemic hydrochloride is first isolated as the least soluble constituent, whilst the mother liquors contain the hydrochloride of the *l*-base which is ultimately purified by repeated crystallisation from moist acetone. The salt melts at 243—245°, and was analysed with the following result :

0·2238 gave 0·1765 AgCl. Cl = 19·51. Calculated Cl = 19·30 per cent.

A solution of 0·1206 gram, made up to 25·1 c.c. with water, gave α_D −0·67 at 16° in a 200 mm. tube: whence $[\alpha]_D$ −69·7° and $[M]_D$ −128°.

d-ac-*Tetrahydro-β-naphthylamine* d-*Camphorsulphonate*, $C_{10}H_{11}\cdot NH_2,C_{10}H_{15}O\cdot SO_3H,\frac{1}{2}H_2O$.

The preceding results indicate that both *d*- and *l*-tetrahydro-β-naphthylamine undergo a partial racemisation during the conversion of their bromocamphorsulphonates into the corresponding hydrochlorides ; it is, in consequence, very difficult to isolate the optically active hydrochlorides in a state of sufficient purity to allow of their proper

characterisation. It seemed probable that the active bases would be most conveniently characterised by means of their more soluble salts with optically active acids, and to this end the salts with Reychler's *d*-camphorsulphonic acid were prepared.

The base was separated from the *d*-bromocamphorsulphonate of $[\alpha]$ +86·5° as described above, and the ethereal solution evaporated to dryness with the corresponding weight of pure *d*-camphorsulphonic acid, the solid residue being subsequently crystallised from hot water. The greater part of the product consists of *d*-tetrahydro-β-naphthylamine *d*-camphorsulphonate, which was easily obtained in a state of purity. It crystallises in long, colourless needles from hot water, and in stout prisms several centimetres in length by spontaneous evaporation of its cold aqueous solution; the crystals contain $\frac{1}{2}H_2O$ and melt at 210—211°. The following analytical results were obtained:

0·3338 air-dried salt lost 0·0078 H_2O at 100. $H_2O = 2·33$.
0·1225 dried salt gave 0·2817 CO_2 and 0·0858 H_2O. C = 62·71; H = 7·78.
0·1168 „ „ 0·2689 CO_2 „ 0·0816 H_2O. C = 62·79; H = 7·77.
0·2530 „ „ 0·1623 $BaSO_4$. S = 8·81.
$C_{20}H_{29}O_4NS$ requires C = 63·32; H = 7·65; S = 8·44; $\frac{1}{2}H_2O = 2·32$ per cent.

A solution of 0·3156 gram of the dried salt, made up to 25·1 c.c. with water, gave α_D +1·20° in a 200 mm. tube at 12·5°; whence $[\alpha]_D$ +47·7° and $[M]_D$ +180·9°. Since Pope and Peachey have shown (Trans., 1899, **75**, 1085) that the *d*-camphorsulphonic ion has $[M]_D$ +51·7°, that of the *d*-tetrahydro-β-naphthylammonium ion should be $[M]_D$ +129·2°; this value agrees well with that obtained above for the molecular rotatory power of *d*-tetrahydro-β-naphthylamine hydrochloride, namely, $[M]_D$ +131·9°.

After the major portion of this salt has separated, the solution begins to deposit *l*-tetrahydro-β-naphthylamine *d*-camphorsulphonate in the characteristic form of colourless scales; this salt owes its formation to the partial optical inversion of the *d*-tetrahydro-β-naphthylamine.

l-ac-*Tetrahydro-β-naphthylamine* d-*Camphorsulphonate*, $C_{10}H_{11}\cdot NH_2, C_{10}H_{15}O\cdot SO_3H, H_2O$.

This salt cannot be conveniently isolated from the mother liquors containing the inversion product of the *d*-base, but was prepared by extracting the base from *l*-tetrahydro-β-naphthylamine *l*-bromocamphorsulphonate with soda and ether, and subsequently evaporating the ethereal solution with the requisite quantity of *d*-camphorsulphonic acid. It crystallises from water in small, colourless scales containing $1H_2O$, and on heating melts first in its water of crystallisation at

83°, and for the second time at 207—208°. The following analytical results were obtained :

1·2016 air-dried salt lost 0·0555 H_2O at 100. $H_2O = 4·61$.
0·1195 dried salt gave 0·2768 CO_2 and 0·0814 H_2O. C = 63·17; H = 7·57.
0·1264 „ „ 0·2920 CO_2 „ 0·0890 H_2O. C = 63·00; H = 7·82.
0·2205 „ „ 0·1403 $BaSO_4$. S = 8·74.
$C_{20}H_{29}O_4NS$ requires C = 63·32; H = 7·65; S = 8·44; $1H_2O = 4·53$ per cent.

A solution of 0·1429 gram of the dried salt, made up to 25·2 c.c. with water at 16°, gave α_D −0·11° in a 200 mm. tube, whence $[\alpha]_D$ −9·7° and $[M]_D$ −36·8°. Since it has aleady been shown that the molecular rotatory powers of the tetrahydro-β-naphthylammonium and camphorsulphonic ions are 130° and 51·7° respectively, *l*-tetrahydro-β-naphthylamine *d*-camphorsulphonate should have the molecular rotatory power $[M]_D$ −68°; the salt was evidently still contaminated with a little of the racemisation product of the *l*-base, its purification from which is very difficult.

l-*Camphorsulphonic Acid and its Salts with the Optically Active Tetrahydro-β-naphthylamines.*

l-Camphorsulphonic acid was prepared from *l*-camphor by the method which Reychler used for the preparation of *d*-camphorsulphonic acid (*Bull. Soc. Chim.*, 1898, [iii], **19**, 120), and was purified by crystallisation from acetic acid and ethyl acetate ; on converting a portion of the product into ammonium salt, the following determination of the rotatory power of the latter showed it to be enantiomorphously related to ammonium *d*-camphorsulphonate, which has $[M]_D$ +51·7° (Pope and Peachey, Trans., 1899, **75**, 1086). A solution of 0·4965 gram, made up to 25·1 c.c. with water at 17°, gave α_D −0·82° in a 200 mm. tube ; whence $[\alpha]_D$ −20·7° and $[M]_D$ −51·6°.

The following two salts were prepared from *d*- and *l*-tetrahydro-β-naphthylamine *d*- and *l*-bromocamphorsulphonates respectively, with the aid of *l*-camphorsulphonic acid, for purposes of comparison with their enantiomorphously related isomerides.

l-ac-*Tetrahydro-β-naphthylamine* l-*Camphorsulphonate*, $C_{10}H_{11}·NH_2,C_{10}H_{15}O·SO_3H,\frac{1}{2}H_2O$.

This salt crystallises from water in long, transparent prisms containing $\frac{1}{2}H_2O$, which is lost at 100°; it melts at 210—211°, and was analysed with the following results :

0·8662 lost 0·0205 H_2O at 100°. $H_2O = 2·36$.
0·1137 dried salt gave 0·2627 CO_2 and 0·0792 H_2O. C = 63·01 ; H = 7·74.

0·1109 dried salt gave 0·2569 CO_2 and 0·0791 H_2O. C = 63·18; H = 7·92.

$C_{20}H_{29}O_4NS$ requires C = 63·32; H = 7·65; $\frac{1}{2}H_2O$ = 2·32 per cent.

A solution of 0·3284 gram of the dried salt, made up to 25·1 c.c. with water, gave α_D −1·24° at 17° in a 200 mm. tube: whence $[\alpha]_D$ −47·4° and $[M]_D$ −179·6°, values in close numerical agreement with those given for the antipodal isomeride.

d-ac-*Tetrahydro-β-naphthylamine* l-*Camphorsulphonate*, $C_{10}H_{11}NH_2,C_{10}H_{15}O{\cdot}SO_3H,H_2O$.

This salt crystallises from water in glistening scales containing $1H_2O$, and, after drying, melts at 207—208°.

0·3268 air-dried salt lost 0·0144 H_2O at 100°. H_2O = 4·41.

0·1185 dried salt gave 0·2753 CO_2 and 0·0833 H_2O. C = 63·36; H = 7·81.

$C_{20}H_{29}O_4NS$ requires C = 63·32; H = 7·65; $1H_2O$ = 4·53 per cent.

A solution of 0·1320 gram of the dried salt, made up to 25·1 c.c. with water, gave α_D +0·14° at 16° in a 200 mm. tube: whence $[\alpha]_D$ +13·3° and $[M]_D$ +50·4°.

d-ac-*Tetrahydro-β-naphthylamine platinichloride*, $2C_{10}H_{11}{\cdot}NH_2,H_2PtCl_6,2H_2O$.

On adding the requisite amount of platinic chloride to an aqueous solution of *d*-tetrahydro-β-naphthylamine *d*-camphorsulphonate acidified with hydrochloric acid, a crystalline precipitate of the platinichloride is obtained; it crystallises from hot, dilute hydrochloric acid in golden-yellow scales which blacken at 235° and melt, with decomposition, at 240°. The salt is practically insoluble in water, and its rotatory power could not be determined.

0·7007 lost 0·0333 H_2O at 100°. H_2O = 4·75.

0·2941 gave 0·0776 Pt. Pt = 26·38.

$C_{20}H_{28}N_2Cl_6Pt$ requires Pt = 26·33; $2H_2O$ = 4·84 per cent.

The Racemisation of d- *and* l-*Tetrahydro-β-naphthylamines.*

It has been proved above that, on preparing the hydrochloride or the camphorsulphonate from *d*-tetrahydro-β-naphthylamine *d*-bromocamphorsulphonate, a certain proportion of the optically active base is inverted; the only alternative to this view is that the original bromocamphorsulphonate is a kind of partially racemic compound containing several equivalents of the *d*-base to one of the *l*-base. That this cannot

be accepted we have proved by treating a pure sample of *d*-tetrahydro-*β*-naphthylamine *d*-camphorsulphonate with soda, extracting with ether, and once more preparing the *d*-camphorsulphonate from the ethereal extract. The salt obtained proved to be a mixture of *d*- and *l*-tetrahydro-*β*-naphthylamine *d*-camphorsulphonates. It follows that, in general, the optically active tetrahydro-*β*-naphthylamines undergo partial racemisation when liberated from their salts by soda and converted into other salts. During which of these two distinct operations the racemisation takes place is not decided; but it is at least probable that it is connected with the liberation of the base, rather than with its recombination, because on preparing a solution of the hydrochloride of known rotatory power, evaporating it to dryness with somewhat less than an equivalent of sulphuric acid, dissolving in water and making up to the original volume, the rotatory power is found to be unchanged. Some kind of momentary tautomerism seems to exist during the liberation of the base from its salts; this tautomerism, however, does not persist after the new salt is formed because no alteration in rotatory power attends the heating of the optically active salts in solution. In the hope that the facility with which racemisation occurs might be applied to the conversion of the externally compensated base into one enantiomorphous component as was done with the compounds containing an asymmetric tin atom (Pope and Peachey, Proc., 1900, **16**, 42, 116), the following experiment was performed. The base was liberated from 20 grams of pure racemic tetrahydro-*β*-naphthylamine hydrochloride by soda and extracted with ether; the ethereal solution was then treated with sufficient *d*-bromocamphorsulphonic acid solution to combine with all the base, and the solution slowly evaporated to dryness. The base was then liberated from the whole by addition of soda and extracted with ether, the ethereal solution being then evaporated and the residual base distilled under about 15 mm. pressure. The pure product thus obtained had the rotatory power α_D +0·05° in a 100 mm. tube. It was once more treated with *d*-bromocamphorsulphonic acid in a sealed tube and the whole heated at 100° for three days, after which the base was liberated, extracted with ether, and distilled under reduced pressure as before. The distillate now had the rotatory power α_D +0·18° in a 100 mm. tube. These results indicated that the externally compensated base was slowly becoming optically active under this treatment, but this might well be because the *l*-base, which remained always dissolved, was more liable to undergo slight oxidation than its *d*-isomeride which was mainly present as solid salt.

d-ac-*Tetrahydro-β-naphthylamine.*

d-Tetrahydro-β-naphthylamine was prepared by treating *d*-tetrahydro-β-naphthylamine *d*-bromocamphorsulphonate of $[\alpha]_D$ +86·5° with a slight excess of soda solution, extracting with ether, drying the ethereal solution with potash, and distilling the base under about 15 mm. pressure. It is a colourless oil which is very viscous and does not fume in the air. One preparation had the rotatory power α_D +30·5° in a 100 mm. tube at 16°, whilst another had the value α_D +37·24° in a 100 mm. tube at 15°. The difference between the rotatory powers of these two preparations indicates that racemisation had taken place to a certain extent.

0·2632 gram of the base of α_D +37·24° was made up to 25·1 c.c. with water containing the calculated quantity of hydrochloric acid; the solution had α_D +0·71° at 15·5° in a 200 mm. tube: whence $[\alpha]_D$ +33·8° and $[M]_D$ +49·8°.

Since we have shown that the *d*-tetrahydro-β-naphthylammonium ion has the molecular rotatory power $[M]_D$ +130°, it follows that, if no racemisation attends the formation of the hydrochloride from the free base, pure *d*-tetrahydro-β-naphthylamine should have a rotatory power of about α_D +96° in a 100 mm. tube, and our best specimen of α_D +37·24° consisted of 70 per cent. of *d*- and 30 per cent. of *l*-base.

Benzylidene-d-ac-*tetrahydro-β-naphthylamine*, $C_{10}H_{11}\cdot N{:}CH\cdot C_6H_5$.

d-Tetrahydro-β-naphthylamine carbonate was precipitated from an ethereal solution of the base obtained by treating the *d*-bromocamphorsulphonate of $[\alpha]_D$ +86·5° with a little more than the equivalent proportion of soda. On heating this carbonate with 1 molecular proportion of benzaldehyde on the water-bath, reaction occurs readily with formation of the benzylidene derivative of the base. On crystallisation from spirit, the product is found to consist of two substances; the less soluble constituent is present in the larger quantity and is the racemic benzylidenetetrahydro-β-naphthylamine prepared from the inactive base by Bamberger and Kitschelt (*Ber.*, 1890, **23**, 876). It crystallises readily in anorthic plates of rhomboidal habit and melts at 51—52°; its identity was established by comparison with the benzylidene derivative prepared from inactive tetrahydro-β-naphthylamine carbonate as described by Bamberger and Kitschelt. It is accompanied by 5 or 10 per cent. of a dextrorotatory isomeride which separates from the mother liquors in spherical aggregates of colourless needles and may be obtained in an apparently pure state by mechanical separation during fractional crystallisation from alcohol.

The purest sample which we succeeded in obtaining melted at 58—60°; it was analysed with the following results:

0·1046 gave 0·3322 CO_2 and 0·0700 H_2O. C = 86·61; H = 7·44.
0·1119 „ 0·3553 CO_2 „ 0·0745 H_2O. C = 86·59; H = 7·40.
$C_{17}H_{17}N$ requires C = 86·81; H = 7·23 per cent.

A solution of 0·3657 gram made up to 25·0 c.c. with absolute alcohol at 18·5°, gave α_D +0·81° in a 200 mm. tube: whence $[\alpha]_D$ +27·6°.

Benzoyl-d-ac-*tetrahydro-β-naphthylamine*,
$C_{10}H_{11}\cdot NH\cdot CO\cdot C_6H_5$.

On treating powdered *d*-tetrahydro-β-naphthylamine *d*-bromocamphorsulphonate of $[\alpha]_D$ +86·5° suspended in water, with benzoyl chloride and soda by the Schotten-Baumann method, benzoylation readily occurs with separation of an oil which immediately solidifies. The product, after preliminary purification in the usual way, is found to be very slightly optically active in alcoholic solution, the specific rotatory power of different preparations varying from 1° to 3°; it consists almost entirely of the inactive benzoyltetrahydro-β-naphthylamine prepared by Bamberger and Müller (*Ber.*, 1888, **21**, 850), and contains but a small proportion of the dextrorotatory benzoyl derivative. A product containing more of the latter compound is obtained by adding benzoyl chloride to an ethereal solution of the base cooled to 0°; after extracting the ethereal solution with water, the tetrahydro-β-naphthylamine hydrochloride recovered from the aqueous solution was found to be still highly dextrorotatory, so that the base unacted upon by the benzoyl chloride does not undergo extensive racemisation. After evaporating the ethereal solution to dryness and fractionally crystallising the residue from dilute acetone, a considerable proportion of it is found to consist of the racemic benzoyl derivative melting at 150—151°, whilst some 5 per cent. or so consists of benzoyl-*d*-tetrahydro-β-naphthylamine. The latter is much more readily soluble than its racemic isomeride, and is ultimately obtained from the acetone solution in felted needles of a woolly appearance; the purest sample obtained melted at 155—157°, and was analysed with the following results:

0·1007 gave 0·2994 CO_2 and 0·0624 H_2O. C = 81·07; H = 6·89.
0·1053 „ 0·3134 CO_2 „ 0·0657 H_2O. C = 81·16; H = 6·93.
$C_{17}H_{17}ON$ requires C = 81·27; H = 6·77 per cent.

A solution of 0·0238 gram, made up to 25·1 c.c. with acetone at 19°, gave α_D +0·11° in a 200 mm. tube; whence $[\alpha]_D$ +58°.

Acetyl-d-ac-*tetrahydro-β-naphthylamine*,
$C_{10}H_{11}\cdot NH\cdot CO\cdot CH_3$.

On adding one-half a molecular proportion of acetyl chloride dissolved in benzene at 0° to a benzene solution of *d*-tetrahydro-β-naphthylamine prepared from the *d*-bromocamphorsulphonate of $[\alpha]_D$ +86·5°, a mixture of the racemic tetrahydro-β-acetonaphthalide melting at 107—108°, which was prepared by Bamberger and Müller (*Ber.*, 1888, **21**, 850), with some 5 per cent. of its dextrorotatory isomeride is obtained. The latter is much more soluble than the racemic compound, and may be separated by continued fractional crystallisation from benzene. It crystallises from the latter solvent in long, colourless needles melting at 104—106°, and on rubbing the crystals with a glass rod they exhibit vivid triboluminescence resembling that of orthobenzoicsulphinide (Pope, Trans., 1895, **67**, 985); this property is lost when the crystals are kept and the racemic compound does not show it at all. The purest sample of the active compound obtained was analysed with the following results:

0·1062 gave 0·2960 CO_2 and 0·0777 H_2O. C = 76·02; H = 8·13.
0·1085 „ 0·3026 CO_2 „ 0·0790 H_2O. C = 76·07; H = 8·09.
$C_{12}H_{15}ON$ requires C = 76·19; H = 7·94 per cent.

A solution of 0·1122 gram, made up to 25·1 c.c. with benzene, gave α_D +0·33° at 16·5° in a 200 mm. tube: whence $[\alpha]_D$ +36·9°.

The Optical Inversion of Amino-compounds.

Although the present investigation was undertaken with a view to further extending the methods available for resolving externally compensated bases, it has led to the observation of a previously unrecorded property which may be exhibited by certain optically active substances, that, namely, of a partial optical inversion attending the liberation of a base from its salts by means of alkali; it has further been found that on preparing the benzylidene, benzoyl, and acetyl derivatives from an active base racemisation may occur, and to a much greater extent than on simply liberating the base from its salts. Two cases of the latter kind are already known: Emil Fischer has shown (*Ber.*, 1900, **33**, 2370) that partial racemisation occurs on benzoylating leucine, $CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, in presence of soda and also on hydrolysing optically active benzoylleucine; Fischer has also shown, (*Ber.*, 1899, **32**, 2466) that considerable inversion takes place on benzoylating optically active glutaminic acid,

$$CO_2H\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H.$$

Tetrahydro-β-naphthylamine is more liable to undergo inversion than

either leucine or glutaminic acid, because racemisation attends the liberation of the former base from its salts, whilst this is not observed with the other two substances.

Fischer's observations, together with our own, allow of some conclusions respecting a branch of knowledge in which stereochemical methods will doubtless ultimately prove of the greatest importance, that, namely, which concerns the mechanism of chemical change. The three bases just mentioned all contain the group $\frac{R'}{R''}\!>\!C\!<\!\frac{H}{NH_2}$; further, salt decomposition and the formation and hydrolysis of acidic derivatives are operations involving the conversion of triad into pentad nitrogen and *vice versâ*. The probable cause of the optical inversion is as follows: The salts of tetrahydro-β-naphthylamine contain pentad nitrogen, and consequently also the group $\frac{R'}{R''}\!>\!C\!<\!\frac{H}{NH_3X}$; when treated with soda, they decompose, with separation of HX, in two ways. The two atomic groups, H and X, may both come from the nitrogen atom, so as to lead to the immediate formation of the stable base, or X may come from the nitrogen and H from the asymmetric carbon atom, leading to the momentary liberation of the transition product, $\frac{R'}{R''}\!>\!C\!:\!NH$, which immediately becomes converted into the stable base by isomeric change. That part of the material which passes through this intermediate stage is necessarily obtained as an externally compensated end-product. This explanation of the partial optical inversion of the base itself is directly applicable, *mutatis mutandis*, to the formation of the much more nearly compensated acidic and benzylidene tetrahydro-β-naphthylamines. A view similar to this has been advanced by Armstrong (Trans., 1900, 77, 1049) to explain the conversion of phenylacetylchloramine into *p*-chloracetanilide and the optical inversion of glutaminic acid.

Further, the environment of the asymmetric carbon atom is certainly tetrahedral, whilst that of the pentad nitrogen atom is probably either that of a pyramid upon a square base or of a double pyramid upon a triangular base, the group X occupying the apex of a pyramid; it would follow that, in the molecule, the distance between H and X attached to the nitrogen atom is of the same order of magnitude as one of the distances between X on the nitrogen atom and the three groups H, R′ and R″, attached to the carbon atom. In the case when H and X attached to carbon and nitrogen respectively are at a distance similar to that separating H and X attached to nitrogen alone, the acid HX would be expected to leave the molecule in both of the two ways indicated above. This case apparently fits that of tetrahydro-β-naphthylamine, leucine, and glutaminic acid;

other substances containing the group $\frac{R'}{R''}>C<\frac{H}{NH_2}$, such as alanine, do not undergo optical inversion, probably because in their additive compounds, R′ or R″, but not H, on the carbon atom, and X on the nitrogen atom, are at a distance apart comparable with that separating H and X attached to the nitrogen atom alone.

The incompatibility of the environments of the tetrad carbon atom and the pentad nitrogen atom may well be responsible for the peculiar course taken by many reactions involving the conversion of triad into pentad nitrogen, and *vice versâ*, reactions such as those concerned, for instance, in the interconversions of isomeric oximes.

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VII.—*The Alkaloids of Corydalis cava. Conversion of Corybulbine into Corydaline.*

By James J. Dobbie, D.Sc., M.A., Alexander Lauder, B.Sc., and Photios G. Paliatseas.

It has been shown in a previous paper (Trans., 1894, 65, 25) that the formula of corybulbine differs from that of corydaline by CH_2, and that the former alkaloid contains only three methoxyl groups, whilst the latter contains four. Having regard to this relation between the formulæ of the two substances, and to the fact that corybulbine is readily soluble in caustic alkalis, in which corydaline is insoluble, and, as shown in this paper, forms an acetyl derivative, the two alkaloids would appear to be related to one another in the same manner as morphine, $C_{17}H_{17}ON(OH)_2$, and codeine, $C_{17}H_{17}ON(OH)\cdot OCH_3$, corydaline being the higher homologue of corybulbine.

The present paper contains an account of the experiments by which this supposed relation was established and the one alkaloid converted into the other.

When corydaline and corybulbine are treated with hydrogen iodide, the methoxyl groups which they contain are replaced by hydroxyl radicles. If corybulbine and corydaline are related to one another in the manner above suggested, the phenolic derivatives yielded by the two alkaloids should be identical. This was found to be the case.

The relation of the two alkaloids to one another having been thus established, the conversion of corybulbine into corydaline by the methods formerly employed in similar cases was next successfully attempted. In 1881, Grimaux converted morphine, $C_{17}H_{17}ON(OH)_2$ into codeine, $C_{17}H_{17}ON(OH)\cdot OCH_3$, by treating it with methyl iodide

in presence of potassium hydroxide (*Compt. rend.*, 1881, **92**, 1140, 1228; **93**, 67, 217) and ten years later, Grimaux and Arnaud converted cupreine, $C_{19}H_{22}N_2(OH)_2$, into quinine, $C_{19}H_{22}N_2(OH)\cdot OCH_3$, by the same method (*Compt. rend.*, 1891, **112**, 766, 1364; 1892, **114**, 548, 672). By similar treatment, corybulbine is converted without difficulty into corydaline. The yield, however, is much larger than that obtained by Grimaux in the case of quinine. The corydaline formed can be isolated without difficulty, since the solubility of corybulbine in sodium hydroxide affords a means of separating any unchanged corybulbine, and the methiodides of both alkaloids being unstable in hot solution, no complication in effecting the separation is caused by their presence. The corydaline thus prepared, and the salts which we have examined, agree in all respects with the natural alkaloid and its corresponding salts.

The position of the hydroxyl group in corybulbine has not yet been definitely ascertained, but the evidence, so far as it goes, points to its presence in the *iso*quinoline nucleus. When corydaline is oxidised with nitric acid, it readily yields corydic acid, $C_{14}H_9N(OCH_3)_2(CO_2H)_2,\frac{1}{2}H_2O$ (Trans., 1897, **71**, 657), which contains an *iso*quinoline nucleus. This acid, on further oxidation, yields, amongst other products, *meta*hemipinic acid, $[(CO_2H)_2:(OCH_3)_2 = 1:2:4:5]$, but no hemipinic acid $[(CO_2H)_2:(OCH_3)_2 = 1:2:3:4]$. Since corydaline on oxidation yields both hemipinic and *meta*hemipinic acids, the benzene ring from which the former acid is derived must be the ring which is destroyed by the oxidation with nitric acid. If the hydroxyl group of corybulbine occurred in this ring, we should expect to obtain corydic acid on oxidising the alkaloid with nitric acid. All attempts, however, to obtain this acid from corybulbine have hitherto failed.

Experimental.

Action of Acetic Anhydride on Corybulbine.

Corybulbine was dissolved in a considerable excess of acetic anhydride, and the solution boiled for 4—5 hours under a reflux condenser. The greater part of the acetic anhydride was then distilled off under reduced pressure, and the concentrated solution set to crystallise in a desiccator. The product, which separated as a thick crystalline crust, was crystallised from carefully dried alcohol, from which it separated in tufts of slender, colourless needles melting at 160°. It was dried over sulphuric acid, and, on analysis, proved to be *acetylcorybulbine*, $C_{18}H_{15}N(OCH_3)_3\cdot O\cdot C_2H_3O$.

0·2676 gave 0·6820 CO_2 and 0·1736 H_2O. C = 69·50; H = 7·20.
$C_{23}H_{27}O_5N$ requires C = 69·47; H = 6·87 per cent.

Action of Hydrogen Iodide on Corybulbine.

The corybulbine was boiled with a strong solution of hydrogen iodide under a reflux condenser until all the methyl iodide was expelled, 2 grams of corybulbine and 20 c.c. of hydrogen iodide being used for each operation. The crystalline solid which separated on cooling was collected by the aid of the pump, well pressed between filter paper, and then recrystallised several times from water. The fine yellow crystals thus obtained were exactly similar in appearance to those of the corresponding substance prepared from corydaline. Both substances behaved in precisely the same way when heated side by side in capillary tubes, melting at about 270° to a clear brown liquid; both dissolve easily in water or alcohol, but only sparingly in ether, and not at all in chloroform. The iodine in the hydriodide obtained from corybulbine was estimated by Carius' method in the substance dried at 100°.

0·2813 gave 0·1496 AgI. I = 28·73.

$C_{18}H_{15}N(OH)_4,HI$ requires I = 28·79 per cent.

Conversion of Corybulbine into Corydaline.

The corybulbine used for this purpose was purified from traces of corydaline by dissolving in potassium hydroxide, in which corydaline is insoluble, and subsequently precipitating with carbon dioxide. It was afterwards repeatedly recrystallised from alcohol. The purified corybulbine, in quantities of 2·5 grams at each operation, was boiled under a reflux condenser for 15—20 hours with the equivalent quantity of methyl iodide and potassium hydroxide dissolved in methyl alcohol. After cooling, the contents of the flask were filtered. The residue was found to consist almost entirely of unaltered corybulbine, which is very sparingly soluble in cold alcohol. The filtrate, which contained corydaline mixed with a small quantity of corybulbine, was evaporated to dryness and dissolved in dilute hydrochloric acid. The corydaline was then precipitated from the acid solution with excess of potassium hydroxide and afterwards boiled repeatedly with the alkali, to get rid of the last traces of corybulbine. The crude corydaline was washed with water until free from alkali, and recrystallised repeatedly from alcohol. Under these conditions we found that from 25 to 30 per cent. of the corybulbine was converted into corydaline. The purified substance was dried at 100° and analysed, with the following results:

0·2515 gave 0·6586 CO_2 and 0·1740 H_2O. C = 71·41; H = 7·68.

0·4088 „ 0·1089 Pt. N = 3·84.

$C_{22}H_{27}O_4N$ requires C = 71·54; H = 7·32; N = 3·79 per cent.

The corydaline thus obtained was carefully compared with the natural alkaloid. Specimens of the two were heated side by side in capillary tubes, and were found to behave in exactly the same way, both of them melting at 135°. The solubilities of the two substances in alcohol, ether, chloroform, benzene, or carbon disulphide were compared, but no difference could be detected between them.

The specific rotatory power was determined, with the following result:

d 20°/4°, 0·7961; c, 0·7251; l, 2 dcm.; $a_D^{20°}$ +4·6°; $[a]_D^{20°}$ +317·1°.

Two determinations of the specific rotatory power of the natural alkaloid gave $[a]_D^{20°}$ = +311° and + 309·5° (Trans., 1895, 67, 17).

Platinichloride of synthetical Corydaline.—The platinichloride of synthetical corydaline was prepared by dissolving the alkaloid in dilute hydrochloric acid and precipitating with platinic chloride. The pale yellow precipitate was collected and washed with cold water till free from acid. It was dried at 100° for analysis:

0·3058 gave 0·0517 Pt. Pt = 16·90.

$(C_{22}H_{27}O_4N)_2,H_2PtCl_6$ requires Pt = 16·97 per cent.

The salt was exactly similar to corydaline platinichloride in appearance, and the behaviour of the two substances, when heated side by side in capillary tubes, was identical. Both softened at 194°, began to decompose at 203°, and were completely decomposed at 210°. The two salts were compared as regards their solubility in water, alcohol, and ether, and were found to agree in all respects.

Ethyl Sulphate of synthetical Corydaline.—This salt is easily prepared by adding a solution of potassium ethyl sulphate to a solution of the sulphate of synthetical corydaline. It forms large, colourless, prismatic crystals, and is identical in appearance with the corresponding salt of the natural alkaloid. The two salts, when heated side by side in capillary tubes, melt between 150° and 160° to a clear yellow liquid. No difference could be detected between the solubility of the two salts; both are easily soluble in hot water, alcohol, or chloroform, but only sparingly so in cold water, and insoluble in ether.

The hydriodides of the natural and artificial alkaloids were also compared and found to be identical.

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VIII.—*Relationships of Oxalacetic Acid.*

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It has been shown by the authors in a previous communication (Trans., 1900, 77, 77) that malic acid, when oxidised by hydrogen dioxide in presence of ferrous iron, gives free oxalacetic acid, and that the latter may readily be isolated by extraction with ether under certain conditions. Some of the properties of the acid were then described, and the present paper gives an account of further studies in this direction. Special attention is given to such reactions as necessitate the use of the free acid rather than its esters, since the latter have been well investigated.

Action of Phenylhydrazine.—It was previously shown that on mixing molecular proportions of phenylhydrazine acetate and oxalacetic acid in aqueous solution, in the cold, the hydrazone is precipitated and is obtained on recrystallisation from ether in the form of colourless, transparent prisms.* This substance when heated turns yellow and decomposes without melting at about 95°, and on crystallising the resulting product from hot alcohol pale yellow needles are obtained which melt at 192°.

It was shown in the previous paper that when the hydrazone of oxalacetic acid is heated with excess of dilute sulphuric acid, it is changed almost immediately into a crystalline mass consisting of 1-phenyl-5-pyrazolone-3-carboxylic acid, identical with that previously obtained from the esters by Wislicenus and by Buchner. No visible evolution of gas occurs in this reaction. It has now been observed that if pure water be substituted for the dilute acid, a brisk evolution of carbon dioxide takes place; the whole goes into solution, and almost immediately a crystalline precipitate separates. This, when recrystallised from alcohol, separates in pale yellow needles which melt at 192°, and is evidently identical with the product obtained by the action of heat alone. It coincides exactly in melting point and other properties with the *hydrazone* of *pyruvic acid*. On analysis the following results were obtained:

* That this is the hydrazone, and not the hydrazide, is proved by its behaviour as a dibasic acid. For example:

0·3940 required 33·9 c.c. of *N*/10 KOH for neutralisation, the calculated amount being 35·5 c.c.

A solution of the substance in dilute alcohol was precipitated with excess of silver nitrate dissolved in the same solvent, the resulting salt being washed, and dried in a vacuum desiccator in the absence of light.

0·2883 gave 0·1428 Ag. Ag = 49·77. $C_{10}H_8O_4N_2Ag_2$ requires Ag = 49·54 per cent.

0·1506 gave 0·3334 CO_2 and 0·0761 H_2O. C = 60·37; H = 5·61.
$C_9H_{10}O_2N_2$ requires C = 60·67; H = 5·61 per cent.

The changes which take place are therefore represented as follows:

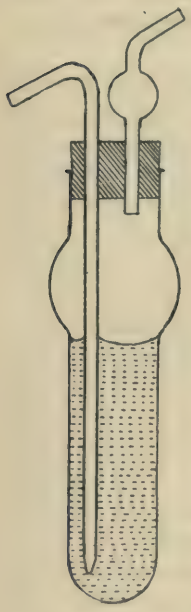
(1) When excess of dilute sulphuric acid is used:

$$C_{10}H_{10}O_4N_2 = C_{10}H_8O_3N_2 + H_2O,$$

(2) when water only is employed:

$$C_{10}H_{10}O_4N_2 = C_9N_{10}O_2N_2 + CO_2.$$

When the concentration of the acid falls below a certain value, both reactions occur simultaneously, and the nature of the change can easily be followed by measurement of the evolved carbon dioxide. Using decinormal sulphuric acid, for example, about 26 per cent. of the hydrazone was found to undergo the second change, and the proportion of carbon dioxide became less and less as more concentrated solutions of the acid were employed, until with acid of about normal strength the amount of gas was not perceptible. Experiments were now made with other acids, using decinormal solutions and making the conditions exactly the same in each case, and it will be seen that the stability of the hydrazone, as regards retention of the 4-carbon molecule, is evidently a function of the concentration of the hydrogen ions. The experiments were made by placing about 0·1 gram of the hydrazone in a tube having a capacity of about 15 c.c., covering it with 7·5 c.c. of the decinormal acid, and heating to boiling for about 2 or 3 minutes in a water-bath. The evolved carbon dioxide was collected in a Lunge's nitrometer, the residual gas swept out of the tube by a current of about 40 c.c. of purified air, and the estimation made by absorption with potash in the usual manner. The accompanying sketch will give an idea of the apparatus employed.



A preliminary experiment was made with pure Iceland spar in order to test the apparatus, and the result showed that the accuracy was well within the limit desired for the purpose, as 0·1065 gram gave 23·6 c.c. of carbon dioxide (corr.), the calculated volume being 23·8 c.c.

The order obtained in the table on p. 93 very closely approximates to that of the relative strengths or 'affinities' of the acids as measured by the well-known methods. In the case of trichloroacetic acid (with regard to which there was at one time a discrepancy), it is probable

that the high result is due to hydrolytic action at the temperature employed.

It would appear, therefore, that the process described affords a very simple method of *comparing* the affinities of acids at 100°, that is, of placing them in 'order of merit.' The exact interpretation of the numbers themselves can scarcely be arrived at from the few and relatively rough determinations here recorded, but the authors hope to make more extended observations in this direction. If it be admitted, as above conjectured, that the results depend upon the concentration of the hydrogen ions, it is easy to understand why the full proportion of carbon dioxide is not obtained even in the case of pure water, since the resulting product is also an acid, and therefore tends to increase the stability of the still undecomposed hydrazone.

Nature of acid.	Weight of substance.	Corrected volume of CO_2.	CO_2 for 1 gram substance.
Nitric	0·0992	1·65	16·6
Hydrochloric	0·0993	1·73	17·4
Sulphuric	0·0990	2·56	25·8
Sulphuric	0·1050	2·84	27·0
Trichloroacetic	0·0980	3·96	50·8
Tartaric	0·0990	6·48	66·9
Malic	0·0990	6·76	68·2
Succinic	0·0998	7·21	72·1
Citric	0·0995	7·30	73·3
Acetic	0·0984	7·72	78·6
[Pure water	0·1200	10·90	90·0]

Action of Hydrazine.—When well cooled alcoholic solutions of oxalacetic acid and hydrazine hydrate are mixed in molecular proportion, the mixture being surrounded by ice and salt, an immediate turbidity is produced and a heavy oil separates which is quickly changed to a hard, white, apparently amorphous mass. This was separated from the liquid, the examination of which will be described below, thoroughly ground with several changes of absolute alcohol and dried in a vacuum desiccator. The yield was about half the weight of acid taken. It dissolves easily in cold water, the solution gives a *red* colour with ferric chloride, and quickly reduces Fehling's solution in the cold. It melts sharply and with violent decomposition at 99°. On analysis, the following results were obtained:

0·1656 gave 0·1614 CO_2 and 0·0835 H_2O. C = 26·58; H = 5·60.
0·1041 „ 28·6 c.c. nitrogen at 18·5° and 734 mm. N = 31·17.
$C_4H_{10}O_4N_4$ requires C = 26·97; H = 5·61; N = 31·46 per cent.

The substance is therefore the *hydrazine salt* of the *hydrazone*, or of

the *hydrazide* of oxalacetic acid, $CO_2H{\cdot}C(N_2H_2){\cdot}CH_2{\cdot}CO_2H,N_2H_4$ or $CO_2H{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}N_2H_3,N_2H_4$.*

When an aqueous solution of this product is heated for a short time in a water-bath it undergoes a marked change. The solution now gives with ferric chloride a very intense *brownish-violet* colour, and after concentration the solution sets to a soft mass which is seen under the microscope to consist of long, transparent prisms. These, after washing with alcohol and drying in a vacuum desiccator, melted at 196°. On analysis, the following result was obtained:

0·1696 gave 58·6 c.c. nitrogen at 20° and 737 mm. N = 39·16.
$C_4H_6O_2N_4$ requires N = 39·43 per cent.

Rothenburg (*Ber.*, 1892, **25**, 3441), by the action of hydrazine hydrate on ethyl oxalacetate, obtained (1) a product easily soluble in alcohol, which is the ester of pyrazolone-3-carboxylic acid, and (2) one nearly insoluble in alcohol which melted at 238°, and had the composition $C_4H_6O_2N_4$. The latter he considers to be the hydrazide of pyrazolone-3-carboxylic acid (Pyrazolon-3-carbonylhydrazin),

$$\begin{matrix} NH{-}N \\ | \quad > CO{\cdot}NH{\cdot}NH_2. \\ CO{\cdot}CH_2 \end{matrix}$$

It appears highly probable that this second product is identical with the one obtained in the present case, although there is considerable discrepancy as to the melting point.

The alcoholic solution which remained after separating the hydrazine salt above described was allowed to evaporate in a vacuum desiccator, and the partly solid residue was treated with cold water. In this way a nearly white, granular residue was left which is very sparingly soluble in cold water, and separates from boiling water in minute crystalline aggregates. For analysis, it was purified by dissolving in alcohol, precipitating with ether and light petroleum, and drying in a vacuum. It turned dark brown, or nearly black, without melting, at about 260—270°. On analysis:

0·1110 gave 0·1514 CO_2 and 0·0353 H_2O. C = 37·20; H = 3·53.
0·1102 ,, 20·9 c.c. nitrogen at 20° and 735 mm. N = 21·46.
$C_4H_4O_3N_2$ requires C = 37·50; H = 3·12; N = 21·87 per cent.

This product therefore corresponds entirely in composition and properties with the *pyrazolonecarboxylic acid* which Rothenburg obtained from the ester above mentioned by hydrolysis with alkalis or concentrated hydrochloric acid.

Action of Hydroxylamine.—When an alcoholic solution of hydroxylamine, prepared by Wohl's method (*Ber.*, 1893, **26**, 730) is mixed

* This composition explains the comparatively small yield, since only one mol. of hydrazine was employed.

with oxalacetic acid, also dissolved in alcohol, in molecular proportion, a turbidity is produced which almost immediately disappears, and the solution after standing for some hours and evaporation in a vacuum desiccator leaves a thick syrup which sets to a white, crystalline mass on stirring or on long standing. This when recrystallised from anhydrous ether melts and decomposes with violent frothing at 133° when gradually heated, or 142—143° if quickly heated. It is very soluble in water or alcohol, but less so in ether; with ferric chloride, the solution gives a brownish or yellow colour. On analysis:

0·1758 gave 0·2135 CO_2 and 0·0550 H_2O. C = 33·12; H = 3·47.
$C_4H_5O_5N$ requires C = 32·65; H = 3·40 per cent.

When the substance is mixed with excess of acetic anhydride or acetyl chloride, it dissolves, and if the resulting solution be allowed to stand for a day or two and then kept in a vacuum desiccator over solid potash and sulphuric acid, the product on treatment with water gives an intense *indigo-blue* colour with ferric chloride.

Piutti (*Chem. Centr.*, 1888, 68; *Gazz.*, 1888, **18**, 457), by the action of the sodium derivative of ethyl oxalacetate upon hydroxylamine hydrochloride, obtained the compound $(CO_2Et)_2{\cdot}CH_2{\cdot}C{:}NOH$, and the compound $CO_2Et{\cdot}CH_2{\cdot}C(NOH){\cdot}CO_2H$ by partial hydrolysis. From the latter, Cramer (*Ber.*, 1891, **24**, 1206) obtained the free acid β-oximidosuccinic acid or the 'oxime of oxalacetic acid.' This melted at 88° and gave a characteristic *blue* colour with ferric chloride.*

Ebert (*Annalen*, 1885, **229**, 76), by the action of nitrous acid on ethyl succinosuccinate, had obtained an acid having the same composition, but this decomposed with frothing at 126°, and gave, with ferric chloride, a brown or yellow colour. Cramer (*loc. cit.*) showed that these two acids are stereoisomerides, and gives reasons for assigning to them the following constitutions (see also Hantzsch, *Ber.*, 1891, **24**, 1192):

α-acid (Ebert's) $\begin{matrix} CO_2H{\cdot}C{\cdot}CH_2{\cdot}CO_2H \\ \| \\ HO{\cdot}N \end{matrix}$ (labile).

β-acid (Cramer's) $\begin{matrix} CO_2H{\cdot}C{\cdot}CH_2{\cdot}CO_2H \\ \| \\ N{\cdot}OH \end{matrix}$ (stable).

By the action of concentrated sulphuric acid, acetyl chloride, or acetic anhydride the α-acid (or its compounds) can be transformed into the β-form, the product then giving the characteristic blue or violet colour with ferric chloride.

It would naturally have been expected that the action of hydroxyl-

* From the somewhat high percentage of carbon in the product obtained in the present case, it is possible that it is not absolutely pure; the numbers, however, are practically identical with those obtained by Cramer, who found C = 33·16 and 33·22; H = 3·10 and 3·16 per cent.

amine upon free oxalacetic acid would give rise to the β-acid, but this evidently is not the case. The properties of the product obtained in the present case closely resemble those of Ebert's α-acid, and the action of acetic anhydride transforms it into a derivative of the β-form. This difference between the behaviour of the free acid and the ethyl ester may possibly be due to the tautomeric difference previously suggested (Michael and Bucher, *Ber.*, 1896, **29**, 1792).

Action of Ammonia.—By mixing together alcoholic solutions of oxalacetic acid and ammonia in different proportions, white precipitates are immediately produced which, after washing with alcohol and drying in a vacuum desiccator, have a composition varying between that required for a normal and an acid salt. If, however, a fairly dilute solution of the acid in absolute alcohol be poured into an excess (slightly more than 3 mols.) of alcoholic ammonia with continuous and vigorous shaking, the precipitate obtained, after washing and drying as before, corresponds in composition to the normal salt.

0·1638 gave 24·9 c.c. nitrogen at 22° and 750 mm. N = 17·27.

$C_4H_4O_5,2NH_3$ requires N = 16·86 per cent.

The salt melts and decomposes at 75—77°, giving a yellow liquid which solidifies to a crystalline mass on cooling. It has a neutral reaction, and gives a deep red colour with ferric chloride. When the ammonium salt is left exposed to the air, it is transformed into a yellow, gummy mass which no longer gives the red colour with ferric chloride.

In order to ascertain whether a further action of ammonia could be induced, the ammonium salt was heated in a stoppered bottle for some hours at 100° with alcoholic ammonia in large excess. A white, crystalline crust of ammonium carbonate was obtained, and a yellow, gummy mass separated at the bottom of the vessel (the alcoholic liquid left only a trace of residue on evaporation). This gummy mass was dissolved in water and acidified with dilute sulphuric acid. A white precipitate was thus obtained which, after washing and drying, melted and decomposed at 273°, gave a reddish-yellow colour with ferrous sulphate and appeared to agree in all respects with the *methylpyridinecarboxylic acid* (m. p. 274°) which Böttinger (*Annalen*, 1877, **188**, 330) obtained by the action of alcoholic ammonia on pyruvic acid.

Action of Urea.—On mixing alcoholic solutions of oxalacetic acid (1 mol.) and urea (rather over 2 mols.) and allowing the mixture to stand in a vessel surrounded by ice, a crystalline precipitate is formed on stirring. This, when washed with alcohol and dried in a vacuum, melts and decomposes at 124° and has the composition of a normal urea salt.

0·1866 gave 23·5 c.c. nitrogen at 17° and 747 mm. N = 14·62.

$C_4H_4O_5,2CON_2H_4$ requires N = 14·58 per cent.

The salt is fairly easily soluble in water and gives a deep red colour with ferric chloride. When heated alone or with phosphorus oxychloride, it yields crystalline products which have not yet been examined.

Action of Aniline.—When ethereal solutions of the acid and aniline are mixed in molecular proportion, a white precipitate is formed which melts at 65—66°. An aqueous solution of this salt remained clear for over a week and gave no precipitate on boiling. If the enolic formula be ascribed to oxalacetic acid, this observation would further confirm the hydroxyfumaric constitution as suggested by Nef and by Michael (compare Michael, *Ber.*, 1886, **19**, 1372; Michael and Bucher, *loc. cit.*).

Action of Benzylphenylhydrazine.—On mixing oxalacetic acid, dissolved in a small quantity of water, with benzylphenylhydrazine dissolved in acetic acid, in molecular proportion, and cooling the mixture with ice, a certain quantity of gummy substance separates at first, but after standing for several hours a nearly white precipitate is obtained. This was collected and washed, first with strong and then with dilute acetic acid, dried in a vacuum desiccator, and crystallised from ether. It melted at 105—106°.

0·1207 gave 10·4 c.c. nitrogen at 18° and 757 mm. N = 10·10 per cent.

The substance is therefore probably not an oxalacetic acid derivative (the benzylphenylhydrazone of which would require N = 8·9 per cent.), but the corresponding hydrazone of *pyruvic acid*, $C_{16}H_{16}O_2N_2$, which requires N = 10·44 per cent.

On using alcoholic solutions of the acid and the hydrazine, a yellow gum is obtained, which never quite solidifies, even on long standing in a desiccator. By treating this with light petroleum and dissolving the residue in ether, a certain amount of yellow, crystalline substance was obtained, but the quantity was too small for examination.

Oxidation of the Acid.—When an aqueous solution of the acid is acted upon by bromine in molecular proportion, a product is obtained, as was previously shown, which gives an intense bluish-violet colour with ferric chloride in presence of caustic alkalis, whilst this on acidification with dilute sulphuric acid is changed to a transient emerald green. The colour-changes, in fact, exactly resemble those given by hydroxymaleic acid with the same reagents (Trans., 1894, **65**, 904). If other solvents, such as acetic acid or ethyl acetate, be employed instead of water, a similar result is obtained, but the violet colour appears more slowly. It is probable that a bromo-acid (bromoxalacetic or bromohydroxyfumaric acid) is first produced and then hydrolysed. On evaporating the acetic acid or ethyl acetate solution in a vacuum, or by extracting the aqueous product with

ether, a thick syrup is obtained which does not crystallise but still gives the ferric chloride reaction.*

A product giving similar colour reaction is obtained when oxalacetic acid is oxidised with the calculated quantity of hydrogen dioxide in presence of ferrous iron, or when malic acid is so oxidised, using nearly two atoms of oxygen to one molecule of the latter acid.

All attempts to isolate this colour-giving acid have so far been unsuccessful. It is evidently very unstable and does not separate under the same conditions as those employed in the isolation of dihydroxymaleic acid nor can it be extracted with ether. The authors are, therefore, inclined to the opinion that it is isomeric and not identical with the latter acid, being probably the ketonic modification,

$$CO_2H{\cdot}CO{\cdot}CH(OH){\cdot}CO_2H.$$

Further light is thrown upon this question by the action of phenylhydrazine. It was shown that the solution obtained by oxidising malic acid in presence of iron gives with phenylhydrazine in the cold a voluminous orange precipitate, which by recrystallisation from hot chloroform is obtained in brilliant orange needles melting at 217—219°. This product gave very constant results on analysis, the mean of four concordant analyses made with distinct specimens, prepared on different occasions, giving,

$$C = 63{\cdot}20\ ;\ H = 5{\cdot}17\ ;\ N = 20{\cdot}16 \text{ per cent.}\dagger$$

These numbers do not correspond to those required for a derivative of oxalacetic acid, but to a more oxidised product, and since no such compound can be obtained by the direct action of phenylhydrazine on oxalacetic acid, it is probable that it is the result of further oxidation by the hydrogen dioxide, which attacks a portion of the oxalacetic acid as fast as it is formed. It can, in fact, be prepared by oxidising oxalacetic acid in presence of ferrous iron, or by adding a further quantity of the dioxide in the oxidation of malic acid, and subsequent addition of phenylhydrazine acetate. Prepared in the latter manner, the recrystallised product melted at 223—224°. On analysis, the following result was obtained:

0·1259 gave 0·2909 CO_2 and 0·0561 H_2O. $C = 63{\cdot}01\ ;\ H = 4{\cdot}94.$

* When excess of bromine was employed and the mixture heated, crystalline plates were obtained which no longer gave the above reaction. They melted at about 92° and gave, on analysis, Br = 64·61 per cent. This product is evidently dibromopyruvic acid, which requires Br = 65·04 per cent.

† The properties of this substance are, in some respects, very similar to those of the osazone of hydroxypyruvic acid discovered by Nastvogel, and in composition the two substances do not differ widely. $C_{15}H_{14}N_4O_2$ requires C = 63·82, H = 4·96, N = 19·85 per cent. The two compounds are, however, at once distinguished by the melting points and by other properties which will be described below.

These numbers correspond to those required for a derivative obtained by the addition of three molecules of phenylhydrazine to one molecule of either dihydroxymaleic or dioxosuccinic acid,* with elimination of three molecules of water.

$C_4H_4O_6 + 3N_2H_3Ph - 3H_2O$ requires C = 63·15 ; H = 5·26 ; N = 20·09 per cent.

$C_4H_2O_6 + 3N_2H_3Ph - 3H_2O$ requires C = 63·46 ; H = 4·80 ; N = 20·19 per cent.

In order to throw light upon the constitution of the compound, the following experiments were made.

The well dried substance was mixed with excess (about ten times its weight) of acetic anhydride and heated on a water-bath, when a considerable evolution of gas took place and a clear, dark coloured solution resulted. The latter, on standing, deposited a mass of orange crystals, which when recrystallised from hot alcohol appeared in the form of beautiful, bright, orange-red needles melting at 149—150°. On analysis :

0·1502 gave 0·3729 CO_2 and 0·0616 H_2O. C = 67·72 ; H = 4·55.

$C_{15}H_{12}ON_4$ requires C = 68·18 ; H = 4·54 per cent.

The composition, melting point, and other properties of this product show that it is identical with that which Knorr obtained by the action of acetic anhydride upon the osazone of hydroxypyruvic acid (*Ber.*, 1888, **21**, 1201), and which Will prepared from the same source by the action of hydrogen chloride in alcoholic solution (*Ber.*, 1891, **24**, 3831). It was also obtained by Knorr (*loc. cit.*) by heating the corresponding pyrazolonecarboxylic acid at its melting point, and was shown by him to be phenylhydrazineketophenylpyrazolone,

$$\begin{matrix} NPh\cdot CO \\ \vert \\ N=CH \end{matrix}\!\!>\!C\cdot N\cdot NHPh.$$

This being a derivative from a 3-carbon acid, it was important to ascertain the nature of the other products of the reaction ; and the experiment was therefore repeated in such a manner that the gaseous product could be displaced by a current of inert gas, the substance being heated with acetic anhydride as before, a current of purified nitrogen passed through the flask, and the product collected in an excess of lime-water. In this way, abundant evidence of the presence of *carbon dioxide* was obtained. After the resulting mixture had been allowed to stand for a day or two, the mother liquor from the crystals was mixed with excess of sodium hydroxide solution and

* That is 'anhydrous' dihydroxytartaric acid, $CO_2H\cdot CO\cdot CO\cdot CO_2H$. Compare Anschütz and Parlato (*Ber.*, 1892, **25**, 1977).

distilled in steam, when a notable quantity of *aniline* was found in the distillate.

These experiments fairly well establish the fact that the substance in question is a 4-carbon derivative, and it must therefore be regarded either as

(1) The dihydrazide-hydrazone of the ketonic acid, $\begin{matrix}CO\cdot CO_2H\\ |\\ CH(OH)\cdot CO_2H\end{matrix}$, tautomeric with dihydroxymaleic acid, or as

(2) The monohydrazide-dihydrazone of dioxosuccinic acid.*

(1) $\begin{matrix}C(N_2HPh)\cdot CO\cdot N_2H_2Ph\\ |\\ CH(OH)\cdot CO\cdot N_2H_2Ph\end{matrix}$ or (2) $\begin{matrix}C(N_2HPh)\cdot CO_2H\\ |\\ C(N_2HPh)\cdot CO\cdot N_2H_2Ph\end{matrix}$.

In the first case, the formation of aniline can easily be explained by the oxidation of the CH·OH group by phenylhydrazine, and the change might be expressed by the equation

$$C_{22}H_{22}O_3N_6 = C_{15}H_{12}N_4 + CO_2 + NH_3.$$

The second formula, however, perhaps better explains the acidic character of the substance (for example, the formation of a crystalline sodium salt when heated with sodium carbonate solution), and in this case the production of aniline must be accounted for in the decomposition of the phenylhydrazine residue by heat (compare Reissert and Kayser, *Ber.*, 1890, **23**, 3703).

In either case, the initial product would be the ketonic acid, $CO_2H\cdot CO\cdot CH(OH)\cdot CO_2H$. It has already been suggested (Fenton, Trans., 1896, **69**, 547) that dihydroxymaleic acid may undergo tautomeric change into this form, and further evidence in this direction will be afforded in a subsequent communication.

Experiments were therefore made in order to ascertain whether the product at present under discussion could be produced from dihydroxymaleic acid.

It has previously been shown (*ibid.*, 548) that by the action of phenylhydrazine on this acid in acetic acid or alcoholic solution, the normal phenylhydrazine *salt* is produced, $C_4H_4O_6,2N_2H_3Ph$. This salt was now heated on a water-bath with excess (about 2 mols.) of phenylhydrazine acetate and water for about 2 hours. The result was an orange-coloured product, which, when recrystallised from hot chloroform, melted at 222° and had all the properties of the malic acid derivative under discussion.

0·1210 gave 20·8 c.c. nitrogen at 20° and 756 mm. N = 19·98 per cent.

* It might, of course, be the phenylhydrazine *salt* of the corresponding pyrazolonecarboxylic acid; but this is improbable from the fact that the sodium salt, when decomposed by hydrogen chloride, gives back a product which melts practically at the same temperature, and appears to be identical with the parent substance.

Reviewing the whole of this evidence, the authors are inclined to prefer the second formula suggested for the substance, that is, to regard it as the monohydrazide-dihydrazone of dioxosuccinic acid, since it seems improbable that the CH·OH group represented in the first formula would resist the action of phenylhydrazine in the experiment last recorded; this formula also agrees somewhat better with the results of analysis.

Summary.

The principal results obtained in the present investigation may briefly be summed up as follows.

Oxalacetic acid by interaction with phenylhydrazine yields the *phenylhydrazone*, $CO_2H{\cdot}CH_2{\cdot}C(N_2HPh){\cdot}CO_2H$, which readily loses carbon dioxide when heated with pure water giving the *hydrazone* of *pyruvic acid*. This decomposition is prevented by acids if the latter are of sufficient concentration, the result in this case being phenylpyrazolone-3-carboxylic acid. By comparing the influence of different acids in this respect, it is easy to compare their relative 'strengths' or 'affinities.'

Hydrazine hydrate gives the *hydrazine salt* of the *hydrazone* $CO_2H{\cdot}CH_2{\cdot}C(N_2H_2){\cdot}CO_2H,N_2H_4$ together with Rothenburg's *pyrazolonecarboxylic acid*. The first named salt when heated with water gives a white, crystalline compound which is probably the *hydrazide* of the latter acid.

Hydroxylamine gives rise to the compound $CO_2H{\cdot}CH_2{\cdot}C(NOH){\cdot}CO_2H$ which contrary to expectation appears to be identical with Ebert's *α-oximidosuccinic acid* and not the *β*-compound. It yields, however, a derivative of the latter by action of acetic anhydride or acetyl chloride.

Ammonia and urea give the respective *normal salts* and the former salt, when heated with excess of alcoholic ammonia, gives a substance corresponding with Böttinger's methylpyridinecarboxylic acid.

When oxalacetic acid is oxidised with hydrogen dioxide in presence of iron, a product is obtained closely resembling dihydroxymaleic acid in properties but which has not yet been isolated. The authors give reasons for considering that this acid has the tautomeric formula $CO_2H{\cdot}CO{\cdot}CH(OH){\cdot}CO_2H$. When treated with phenylhydrazine, this product gives a bright orange compound melting at 222—224°. The latter has been the subject of an exhaustive examination and the evidence leaves little room for doubt that it is the hydrazide-dihydrazone of dioxosuccinic acid.

IX.—*Interaction of Urethanes and Primary Benzenoid Amines.*

By Augustus Edward Dixon, M.D.

In a paper published some years ago (Trans., 1895, **67**, 562), the author gave, incidentally, a brief account of *ab*-phenyl-*p*-tolylcarbamide; this substance was prepared from phenyl *iso*cyanate and *p*-toluidine, the melting point of a specimen only once recrystallised being 212—213° (corr.). The writer regarded the compound as new, having overlooked descriptions of it given by Huhn (*Ber.*, 1886, **19**, 2408), who records the melting point as 211°, and by Goldschmidt and Meissler (*Ber.*, 1890, **23**, 273); the latter chemists obtained it by heating *p*-tolyl *iso*cyanate with thiocarbanilide, and give the melting point as 211° also; whether corrected or otherwise is not mentioned in either case.

These descriptions appear to have escaped the notice of Manuelli and Comanducci, who state in a recent paper (*Gazz.*, 1899, **29**, ii, 142) that it is produced by heating phenylurethane with *p*-toluidine; a complete analysis is appended, and the melting point given as 259—260°.

With a view to ascertain the cause of this discrepancy, some experiments were undertaken, of which an account is given below.

Amongst the acidic derivatives of urea, isomeric forms are now known to exist (compare Trans., 1899, **75**, 375), and it struck the writer as just possible that the substance melting at 260° might be a 'labile' form of the symmetrical carbamide, for instance, $PhN{:}C(OH)\cdot NH\cdot C_7H_7$. The probability, however, of this being the explanation was slight, considering that phenylurethane and aniline yield ordinary carbanilide, $CO(NHPh)_2$, and not an isomeride (Wilm and Wischin, *Annalen*, 1868, **147**, 160); moreover, the writer observed some years ago that the (sec.)-dibutylcarbamide produced from butylurethane and butylamine (Trans., 1895, **67**, 561) is identical with that obtained by desulphurising *ab*-(sec.)-dibutylthiocarbamide with silver nitrate.

Before examining the interaction between phenylurethane and *p*-toluidine, it was decided to once more verify the melting point of *ab*-phenyl-*p*-tolylcarbamide, notwithstanding that Paal and Vanvolxem have also recorded it as 212° (*Ber.*, 1894, **27**, 2426); their preparation was made from phenyl *iso*cyanate and *p*-toluidine, but it is not stated whether the melting point was corrected.*

* It is hardly necessary to remark that, at these somewhat high temperatures, the correction is occasionally considerable, amounting to several degrees; the melting points recorded by the writer in the present paper are all corrected for the exposed thread of mercury.

The urea was this time prepared by desulphurising the corresponding thiocarbamide (from phenylthiocarbimide and *p*-toluidine, m. p. 141—142°) with silver nitrate. After recrystallisation from boiling alcohol, the substance was pure white, and melted at the temperature previously recorded, namely, 212—213°; it occurred in long, flexible, flattened needles, having a brilliant, silvery lustre, becoming electrical on friction, and afforded, by wet combustion, 74·32 per cent. of carbon, against 74·29, calculated for $C_{14}H_{14}ON_2$. It should be added that the melting point of this specimen, when several times recrystallised from alcohol, rose somewhat, becoming eventually constant at 215°.

In the experiments with bases and urethanes, the method first adopted was to heat exactly equivalent proportions of the constituents in a sealed tube; but on learning subsequently that Manuelli and Comanducci had boiled them together in an open vessel under a reflux condenser, their preparations were carefully repeated under the prescribed conditions.

Phenylurethane and p-*Toluidine.*—A very slight excess of the urethane was taken, the mixture being heated in a paraffin bath at about 185° for 3 hours, using a tube as condenser. The product, when cold, formed a greenish-brown, friable, crystalline mass, penetrated by a dark oil. After washing with water acidified with hydrochloric acid, and then with spirit and ether, it became white; the yield of dry product amounted to something over 40 per cent. of the weight of materials employed. It was dissolved in the least possible quantity of boiling alcohol, in which it is rather sparingly soluble; on cooling, a felted mass of pearly crystals was obtained, resembling thiocarbanilide in appearance, and becoming highly electrical on friction; the mother liquor gave a second crop of the same substance melting at 260—261°. Presently a third crop of crystals separated, in flattened white needles, becoming moist at 212°, and melting, rather indistinctly, between 213° and 216°. This was no doubt phenyl-*p*-tolylcarbamide, containing a little of the substance of higher melting point; a fourth crop melted at 213—214°, and was, consequently, the real phenyltolyl compound, practically pure, but the amount was not enough for analysis.

The nitrogen in the substance melting at 260—261° was estimated:

0·2 gave 20·4 c.c. nitrogen at 17° and 760 mm. N = 11·83 per cent.

Another determination gave 11·75 per cent.; these figures are too low for phenyltolylcarbamide, or its possible isomeride, which would require N = 12·43 per cent.

An examination of the oil, removed from the original crude product, showed it to contain a large amount of *aniline*. Once in possession of this fact, the course of the interaction becomes easy to understand;

the *p*-toluidine, even though present in less than equivalent proportion, attacks to a greater or less extent the phenyltolylcarbamide first produced, the interactions running as follows:

(I). $PhNH\cdot CO\cdot OEt + C_7H_7\cdot NH_2 = PhNH\cdot CO\cdot NH\cdot C_7H_7 + EtOH.$

(II). $PhNH\cdot CO\cdot NH\cdot C_7H_7 + C_7H_7\cdot NH_2 = PhNH_2 + CO(NH\cdot C_7H_7)_2.$

The substance melting at 260—261° is thus di-*p*-tolylcarbamide (melting point 260°, Manuelli and Ricca-Rosellini, *Gazz.*, 1899, **29**, ii, 124); this requires N = 11·70 per cent.; the nitrogen found, as just stated, amounted to 11·83 and 11·75 per cent.

A similar experiment was also performed in a sealed tube; in the first case, 14 grams were heated for 3 hours at 200°; in the second, 17 grams for 4 hours at 210°, the latter giving a much better yield. Aniline was formed, together with a solid, which began to soften at 250°, and was melted at 256°; by recrystallisation, this yielded di-*p*-tolylcarbamide, softening a little at 259°, and melting at 260—260·5°; the mother liquor gave a crop of needles, melting, after a couple of recrystallisations, at 211—212°, and consisting of phenyl-*p*-tolylcarbamide.

p-*Tolylurethane and Aniline.*—In this converse experiment, the above constituents were heated, under pressure, for 3 hours at 220—230°, the urethane being in very slight excess. Washing with spirit removed the adherent oil, and left a white solid, melting, somewhat indistinctly, at about 205—206°; this was eventually resolved into a main quantity of phenyl-*p*-tolylcarbamide melting at 213—214° (found N = 12·3 per cent.), and a minimal quantity of a substance melting at about 256—257°, probably di-*p*-tolylcarbamide, but the amount was insufficient for complete purification and analysis, only about 0·2 gram being obtained from 10 grams of material. In this case, no doubt, the aniline at first expels some *p*-toluidine from the phenyl-*p*-tolylcarbamide, the change reversing itself to some extent with the free *p*-toluidine when the large excess of aniline has been diminished by interaction with the urethane.

This experiment was also repeated by boiling the constituents in an open vessel, but no difference worth recording was observed in the phenomena, save that the only product isolated was the phenyl-*p*-tolyl compound (m. p. found, 211·5—212·5°). From the above results it would appear that *p*-toluidine is much more active in expelling aniline than *vice versâ*.

Phenylurethane and o-*Toluidine.*—Two experiments were made under pressure, the mixture in one case being heated for about half an hour at 270°, in the other, for three hours at 220°; no material difference was observed in the results. A dark-coloured solid was obtained, mixed with an oil, which gave the reactions of aniline; the former

became white on washing with alcohol and ether; it began to shrink at 224°, and melted, indistinctly, between 226° and 229°. It was boiled with a quantity of alcohol insufficient to dissolve it completely, and the residue (which now shrank a little at 239° and melted about 242—243°), was recrystallised from the same solvent. It is rather sparingly soluble, and was deposited on cooling in slender, vitreous prisms melting at 249—250°.

Obviously this substance could not be phenyl-*o*-tolylcarbamide, whose melting point, according to Huhn (*Ber.*, 1886, **19**, 2410), lies at 212°, or carbanilide (m. p. 238°); presumably, therefore, it was di-*o*-tolylcarbamide. The melting points given by various observers for this compound are too divergent to be of much use for identification, but a nitrogen determination gave figures agreeing with those required for the ditolyl derivative, $CO(NH\cdot C_7H_7)_2$:

Found N = 11·97. $C_{15}H_{16}ON_2$ requires N = 11·70 per cent.

Out of the alcoholic extract, exceedingly fine needles separated in woolly-looking clumps; after a couple of recrystallisations they became soft at 202° and melted at 203—204°; they proved to consist of nearly pure phenyl-*o*-tolylcarbamide:

Found N = 12·6. $C_{14}H_{14}ON_2$ requires N = 12·43 per cent.

An experiment made by heating the constituents together at 185° in a reflux apparatus for 4 hours gave similar results, save that a rather larger proportion of the phenyl-*o*-tolyl derivative was obtained.

The melting point just recorded for the latter compound lies a good deal below that given by Huhn, who obtained the substance (*loc. cit.*) from carbophenyl-*o*-tolylimide and weak alcohol; this lowness, it seemed, might be due to the presence of traces of di-*o*-tolylcarbamide, since the latter is less soluble in alcohol than phenyl-*o*-tolylcarbamide; however, to make certain, the compound was again prepared, first by desulphurising *ab*-phenyl-*o*-tolylthiocarbamide (m. p. 142°) with silver nitrate, and next by combining phenyl *iso*cyanate with *o*-toluidine. When several times recrystallised from strong alcohol, both products were deposited in very minute needles melting at 207—208°.

Found N = 12·5. $C_{14}H_{14}ON_2$ requires N = 12·43 per cent.

Phenyl-α-naphthylcarbamide.—Amongst other compounds described in Manuelli and Comanducci's paper is a symmetrical phenyl-α-naphthylcarbamide, obtained from α-naphthylamine and phenylurethane; it is said to blacken at about 274°, and melt at 277—278°. In order to verify this statement, the carbamide was prepared, first, by desulphurising the corresponding thiocarbamide (m. p. 163°) with silver nitrate, and next, by combining phenyl *iso*cyanate and α-naphthyl-

amine in dry benzene. The latter method gave a pure white solid: after three recrystallisations from a mixture of benzene and alcohol, it occurred in snowy-white, silky, microscopic needles, which softened at 223°, as if about to melt; they did not fuse, however, but at 224° hardened again. On raising the temperature, the substance gradually darkened from about 230°, and became moist, until at about 244° it melted, evolving gas. If put into the melting point apparatus at or above 223°, it melts to a water-clear liquid, resolidifying almost immediately; if put in only two or three degrees below this temperature, it melts, becoming clear, on reaching it; in a moment, however, it resolidifies, and now melts, somewhat indistinctly, at the higher temperature, to a black liquid.

The specimen prepared by the former method retained, even after several recrystallisations, a very faint buff tinge; its behaviour on heating was, however, similar to that of the *iso*cyanate product, save that its melting point was a degree lower, namely, 222°.

Found N = 10·88; $C_{17}H_{14}ON_2$ requires N = 10·64 per cent.

The properties just described do not agree very satisfactorily with those attributed by Manuelli and Comanducci to phenylnaphthylcarbamide; it was, of course, possible that the not very marked softening at 223° might have escaped their notice, but even if so, there still remained a large discrepancy. In order to clear the matter up, their experiment was repeated.

Phenylurethane and α-Naphthylamine.—Equal weights, as prescribed (corresponding to over 15 per cent. of base in excess of the calculated quantity), were heated in a paraffin-bath at 220—230°. In about half an hour, solid matter began to appear, and before an hour had elapsed the contents of the flask were apparently solid; the heating was continued, however, in accordance with the directions, for nearly three hours. When cool, the product was broken up, and washed with dilute hydrochloric acid; from the washings, by treatment with excess of alkali, a colourless liquid was precipitated; this was extracted with ether, and remained on evaporation of the latter, as a yellowish oil, which gave all the reactions of aniline, and was further identified by the production, with phenylthiocarbimide, of thiocarbanilide.

The residue was ground up in a mortar with cold spirit, filtered, washed with more spirit until practically colourless, and then boiled with a large volume of alcohol; as it proved to be nearly insoluble in this solvent, the mixture was filtered whilst still hot, and the residue, which was now snow-white, examined. It formed a microcrystalline powder, becoming highly electrical on friction; when heated in a capillary tube, it showed no sign of change up to about 270°, when it began to darken a little; neither, when put into the apparatus

at 230° or 240°, did it melt or soften. At 283°, it darkened greatly, and melted at 286—287°, with effervescence, to a black liquid.

The anticipation that this compound would prove to be dinaphthylcarbamide, $CO(NH\cdot C_{10}H_7)_2$, was confirmed by the results obtained on making a complete analysis:

Found C = 80·78; H = 5·16; N = 9·24.
$C_{21}H_{16}ON_2$ requires C = 80·75; H = 5·14; N = 9·00 per cent.

Appended are the figures required for phenylnaphthylcarbamide, together with those obtained by Manuelli and Comanducci; the writer is unable to explain the discrepancy, but recognises that their data entirely justify the conclusions at which they arrived:

Calculated for $C_{17}H_{14}ON_2$, C = 77·86; H = 5·34; N = 10·64 per cent.
Found ..... C = 77·52; H = 5·68; N = 10·51 „ „

The alcoholic washings from the above compound, when diluted with water, gave a small quantity of a purplish solid; after a couple of recrystallisations from alcohol, using animal charcoal, the substance was obtained in masses of woolly needles, still retaining a very faint pinkish tinge; they melted about 221°, resolidifying quickly, and commencing then to darken at about 230°; the amount was barely sufficient for analysis, but the compound was obviously phenyl-*α*-naphthylcarbamide, nearly, but not quite, pure.

In connection with the various results detailed above, it may be noted that Manuelli and Comanducci have also described a symmetrical phenylamylcarbamide, obtained from phenylurethane and amylamine, and separating, after numerous recrystallisations, from dilute alcohol, in slender white prisms melting at 238°.

Now all the known symmetrical disubstituted ureas containing one phenyl, together with one purely fatty, radicle, melt at temperatures far below this; in the appended list of such compounds, $CO<^{NHPh}_{NHR}$, the variable radicle, R, alone is given.

Radicle.	M. p.	Radicle.	M. p.
CH_3	151°	$(C_2H_5)_2CH\cdot CH_2$	70°
C_2H_5	100	$C_2H_5\cdot C(CH_3)_2\cdot CH_2$	103—105
$C_2H_5\cdot CH(CH_3)$	156	C_9H_{19}	63
$(CH_3)_3C\cdot CH_2$	155	$C_{17}H_{35}$	99

Moreover, normal amylamine is stated to have been employed in preparing the phenylamylcarbamide in question: in this case, the melting point might be expected to lie below 155° (that of phenyl-

*iso*amylcarbamide), instead of 83° above it. It seems not impossible that this interaction runs a course resembling that between aniline and *p*-tolylurethane (p. 104); and that the supposed phenylamylcarbamide is really carbanilide, which, according to Young and Clark (Trans., 1898, **73**, 367), melts at 238—239°. This, however, is a mere conjecture, the writer having no opportunity of carrying out the experiment with normal amylamine, and is advanced with reserve, in view of the analytical evidence which Manuelli and Comanducci have brought forward in support of their statements.

Summary.

Phenylurethane, when heated with an equivalent proportion of *o*- or *p*-toluidine, or with α-naphthylamine, yields in each case a symmetrical (mixed) disubstituted carbamide containing one phenyl group, together with a group derived from the base used; this product is always accompanied by the corresponding (simple) disubstituted carbamide containing the radicle of the base alone: with α-naphthylamine, little but dinaphthylcarbamide is obtained; with *p*-toluidine, the simple carbamide also largely preponderates; with *o*-toluidine, the proportion of ditolylcarbamide obtained in the mixture is considerably lower. The simple carbamide is less soluble than the mixed, in the cases mentioned; consequently the process is not a satisfactory one for the preparation of such mixed derivatives in a state of purity.

p-Tolylurethane and aniline yield mainly *ab*-phenyl-*p*-tolylcarbamide: a secondary product, obtained in very limited quantity, appeared to be di-*p*-tolylcarbamide.

Experimental reasons are assigned for concluding that the phenyl-*p*-tolylcarbamide and phenyl-α-naphthylcarbamide of Manuelli and Comanducci (*Gazz.*, 1899, **29**, ii, 136) are di-*p*-tolyl- and di-α-naphthylcarbamide respectively.

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X.—*Infracampholenic Acid, an Isomeride of Campholytic and* iso*Lauronolic Acids.*

By MARTIN ONSLOW FORSTER.

EIGHTEEN months ago I described the unsaturated nitrile, $C_9H_{13}N$, produced on eliminating hydrogen bromide and carbon monoxide from the anhydride of bromonitrocamphane (Trans., 1899, **75**, 1141). At that time it seemed highly probable that the nitrile, and the amide

obtained from it on hydrolysis, were derivatives of Walker's campholytic acid, because the amide, although distinct from *iso*lauronolamide, was converted into that substance by dilute mineral acids.

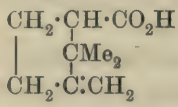
The investigation of the acid derived from the amide is still incomplete, but the recent appearance of a posthumous paper by Tiemann, in association with Kerschbaum and Tigges, on the two campholytic acids (*Ber.*, 1900, **33**, 2935), closely following a communication on the same subject by G. Blanc (*Bull. Soc. Chim.*, 1900, [iii], **23**, 695), obliges me to describe briefly the progress which has been made in the examination of the substance.

The nitrile has to be heated with alcoholic potash continuously for several weeks before ammonia ceases to be evolved; there is then obtained the potassium salt of a liquid acid, $C_9H_{14}O_2$, which closely resembles Walker's campholytic acid, forming a viscous oil which boils at 145° and 239° under pressures of 24 mm. and 758 mm. respectively. Moreover, the substance is optically inactive, and treatment with dilute mineral acids transforms it into *iso*lauronolic acid, differing in no respect from the acid obtained by the action of aluminium chloride on camphoric anhydride. Here, however, the resemblance to campholytic acid ceases. According to Walker (Trans., 1893, **63**, 498), that substance absorbs a molecular proportion of bromine, yielding the dibromide $C_9H_{14}O_2Br_2$, which melts and blackens at 106—107°. When, however, the new acid is treated with bromine under the conditions specified by Walker, two molecular proportions of the halogen are engaged, hydrogen bromide is eliminated, and the solid product consists of a tribromocarboxylic acid, $C_9H_{13}O_2Br_3$, which melts to a colourless liquid, and evolves gas, at 182°. Moreover, the dibromide of the new acid, which can be obtained when bromine is slowly added in quantity scarcely sufficient to convert all the substance into the compound $C_9H_{14}O_2Br_2$, is quite distinct from the isomeric dibromide of campholytic acid, because it melts at 125° without blackening. Furthermore, whilst campholytic acid is converted by hydrobromic acid into the hydrobromide, $C_9H_{15}OBr$, several attempts, under varying conditions, to obtain a corresponding derivative from the new acid have resulted in the production of *iso*lauronolic acid.

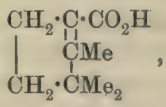
It has now been shown that the new substance is the lower homologue of α-campholenic acid, and I propose therefore to call it infracampholenic acid, the prefix "infra" representing in this sense the converse of "homo."

Some months after the discovery of tribromodihydroinfracampholenic acid, and the consequent recognition of the fact that infracampholenic and campholytic acids are distinct, the paper by G. Blanc (*loc. cit.*) was published without any previous intimation that he proposed to

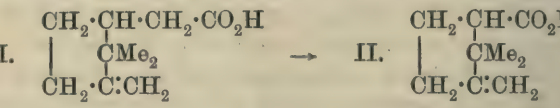
investigate the nitrile with which I was working. On reducing that substance with sodium in absolute alcohol, Blanc obtained the amine which α-campholenamide yields when oxidised with sodium hypobromite, namely, α-aminocampholene, first described by Blaise and Blanc (*Bull. Soc. Chim.*, 1899, [iii], **21**, 976); assuming that the nitrile is indeed the nitrile of campholytic acid, this result appeared to confirm the view that campholytic acid is the lower homologue of α-campholenic acid, and Blanc would have expressed its constitution by the formula



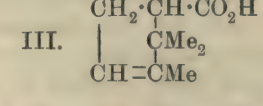
but for the appearance of Walker's latest paper on the subject (Trans., 1900, **77**, 374). In consequence of this publication, Blanc agreed that campholytic acid is a stereoisomeride of *iso*lauronolic acid,



and adopting Bouveault's formula for α-campholenic acid, I, represented the constitution of infracampholenic acid by the expression II:



Working with Noyes' active campholytic acid, that is to say, with the acid obtained by the action of nitrous acid on dihydroaminocampholytic acid, Tiemann (*loc. cit.*) arrived at αα-dimethyltricarballylic acid by oxidation with dilute nitric acid, and therefore represents the constitution of campholytic acid by the formula III:



This view is now endorsed by Blanc (*Compt. rend.*, 1900, **131**, 803), who has oxidised inactive campholytic acid, derived on this occasion from *iso*lauronolic acid by Walker's process, obtaining also αα-dimethyltricarballylic acid.

In giving expression to this change of view, Blanc does not refer to the result of his experiment with the nitrile of infracampholenic acid, which showed that this acid is the lower homologue of α-campholenic acid; the formula III, which, in agreement with Tiemann, he ascribes to campholytic acid, represents the latter substance as the lower

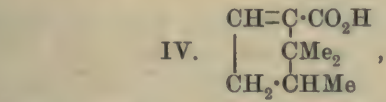
homologue of α-campholenic acid, the constitution of which is best expressed by Tiemann's formula,



In view of the fact, established in this paper, that campholytic and infracampholenic acids are distinct, one of three things follows: Tiemann's formula for α-campholenic acid is incorrect, Blanc's reduction of infracampholenonitrile to α-aminocampholene is misleading, or the expression III does not truly represent the structure of campholytic acid.

Now Tiemann's formula for α-campholenic acid is based on the production of *iso*ketocamphoric acid, $COMe\cdot CMe_2\cdot CH(CH_2\cdot CO_2H)_2$, on oxidation, and appears therefore to be well founded. There is likewise no reason to mistake the conclusion to be drawn from Blanc's experiment showing that α-campholenic acid is the homo-derivative of infracampholenic acid. There remains, therefore, the third possibility, namely, the invalidity of the formula for campholytic acid advocated by Tiemann and by Blanc.

While discussing the constitution of that substance, the last-named investigators do not allude to the alternative formula,



from which, by oxidation, αα-dimethyltricarballylic acid might be obtained. Perhaps the drawback which presented itself to them was the conversion of the complex $\cdot CMe_2\cdot CHMe\cdot$ into the grouping $\cdot CMe_2\cdot CH(CO_2H)\cdot$, a change which is certainly unusual. In view of the present difficulty, however, this formula deserves consideration because the structure of infracampholenic acid would then be represented by the expression III.

The following arguments may be brought forward in support of this suggestion.

1. The formula IV, with the qualification already mentioned, accounts for the production of αα-dimethyltricarballylic acid,



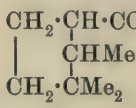
2. It represents campholytic acid as an αβ-unsaturated acid, in accordance with the results of Walker's experiments.

3. It reconciles the facts that infracampholenic acid is distinct from

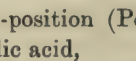
campholytic acid, and is nevertheless a lower homologue of α-campholenic acid.

4. The representation of infracampholenic acid by the formula III explains the production of a tribromo-derivative by direct action of bromine, the α-carbon atom being hydrogenised, and therefore susceptible to the action of bromine.

5. The formula IV is more consistent with the behaviour of campholytic acid towards bromine than the representation which is given by Tiemann and by Blanc, because dihydro*iso*lauronolic acid,

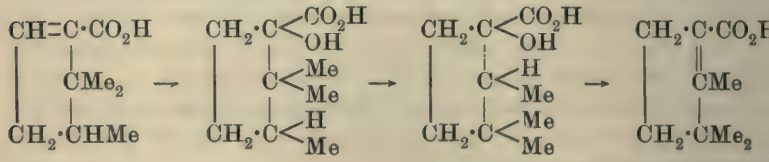


can be brominated in the α-position (Perkin, Trans., 1898, **73**, 838), and tetramethylenecarboxylic acid,



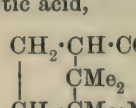
readily undergoes the same change (Perkin and Sinclair, Trans., 1892, **61**, 42); if therefore, campholytic acid has the structure III, it might be expected to behave like infracampholenic acid, and give a tribromo-derivative instead of a dibromide.

6. On the lines of Lapworth's proposal, according to which the production of *iso*lauronolic acid from camphoric acid involves the migration of a methyl group (Trans., 1900, **77**, 1057), the conversion of campholytic acid into *iso*lauronolic acid can be explained as follows:



this scheme is no less plausible than that adopted by Blanc (*Compt. rend.*, 1900, **131**, 805; Abstr., 1901, **80**, i, 11) for the same purpose.

Against the propositions made in this paper will be urged the fact that aminodihydrocampholytic acid,



under the influence of nitrous acid, is more likely to yield a substance having the formula III than the alternative compound, IV. This is, *primâ facie*, true, but it must be borne in mind that the substituents

in this complex display great mobility, which is shared by the hydrogen atoms.

In the hope of settling definitely the constitution of infracampholenic acid, a study of its products of oxidation is being made, and I expect to gain evidence of its structure also by examining the alcohol obtained from aminoinfracampholene, $C_8H_{13}\cdot NH_2$, by the action of nitrous acid; the base itself is described in this paper, being readily furnished by infracampholenamide when treated with sodium hypobromite.

Before proceeding to the experimental details, I think it is desirable to draw attention to the nomenclature for campholytic and *iso*lauronolic acids adopted by Tiemann's collaborators in the paper first mentioned (*Ber.*, 1900, **33**, 2935). They distinguish these substances, which are perfectly well recognised under the original names, as α- and β-campholytic acids respectively. This distinction seems to be somewhat unfortunate. In the first place, the substance which they propose to call α-campholytic acid, is derived from β-camphoramic acid, whilst α-camphoramic acid yields, not β-campholytic acid, but lauronolic acid. Secondly, it is claimed that the use of these letters illustrates the relationship of the acids to α- and β-campholenic acids; no evidence is adduced in the paper, however, to show that such a relation holds good, and although Blanc's investigations suggest that β-campholenic acid is the homo-derivative of *iso*lauronolic acid, the same author has shown that α-campholenic acid is not connected with campholytic acid in a similar manner. In these circumstances, confusion will be avoided by adherence to the original names for campholytic and *iso*lauronolic acids.

Experimental.

Infracampholenic Acid, $C_9H_{14}O_2$.

The readiness with which the amide, $C_8H_{13}\cdot CO\cdot NH_2$, is converted into *iso*lauronolamide under the influence of dilute hydrochloric acid renders this agent useless for the purpose of hydrolysis. Attempts have been made under varied conditions to transform the amide into the acid by means of nitrous acid, but on each occasion the unchanged substance was recovered. The only alternative was to use alcoholic potash, and although the action is extremely slow, and involves heating the liquid during several weeks, this method was ultimately adopted.

Twenty grams of the purified amide were dissolved in 100 c.c. of alcohol, and heated with 25 grams ($3\frac{1}{2}$ mols.) of potassium hydroxide dissolved in the minimum quantity of water, until no further evolution of ammonia took place. Hydrolysis was complete after 200 hours. The liquid was then evaporated on the water-bath, and the viscous residue washed two or three times with ether, dissolved in water, and

just acidified with cold, dilute, hydrochloric acid, which precipitated a pale brown, viscous oil. This was dissolved at once in ether, washed with water, redissolved in sodium carbonate, and then extracted with ether in order to remove any non-carboxylic impurities. The solution of the sodium salt was exactly neutralised with dilute sulphuric acid, and on removing the precipitated oil with ether, drying the extract with fused sodium sulphate, and afterwards evaporating the solvent on a water-bath, 19 grams of the acid were obtained. The product, which was pale brown and very viscous, was then distilled under reduced pressure ; various specimens boiled at 145°, 170°, 180°, and 239° under pressures of 24 mm., 60 mm., 105 mm., and 758 mm. respectively, yielding a colourless, or very pale yellow, viscous oil, having a faint, somewhat disagreeable odour.

0·2000 gave 0·5122 CO_2 and 0·1630 H_2O. C = 69·85 ; H = 9·05.
$C_9H_{14}O_2$ requires C = 70·13 ; H = 9·09 per cent.

A 20 per cent. solution in ether is optically inactive, and a 10 per cent. solution of the amide in absolute alcohol is also devoid of activity. The acid has a sp. gr. 1·0146 at 16°, and a refractive index μ^{Na} 1·4660 at 19°.

When infracampholenic acid is warmed with dilute sulphuric acid it soon solidifies, yielding *iso*lauronolic acid, which was compared with a specimen obtained from camphoric anhydride ; it melts at the same temperature, and like the acid from this source, is optically inactive.

Certain salts of infracampholenic acid are well defined. A neutral solution of the ammonium salt gives no precipitate with magnesium sulphate, calcium chloride, or barium chloride, but the *mercuric* salt forms minute white needles, sparingly soluble in cold water. The *copper* salt separates immediately as a dark green, crystalline precipitate, which dissolves readily in hot alcohol, forming a deep green solution ; this deposits nodular aggregates of minute green needles. The *lead* salt forms a white, flocculent precipitate, soluble in boiling water, from which it crystallises in small, transparent, six-sided plates. The *silver* salt is soluble in hot water, separating in colourless crystals which are affected only slowly by light.

Tribromodihydroinfracampholenic Acid, $C_9H_{13}O_2Br_3$.

In the first attempts to prepare a dibromide, the conditions prescribed by Walker (*loc. cit.*) were observed. Seven grams of bromine dissolved in 20 c.c. of dried carbon disulphide were placed in a wide-mouthed bottle through the stopper of which passed a tap-funnel and a tube containing calcium chloride ; the bottle was immersed in melting ice in a large, blackened beaker. Five grams of infracampholenic

acid dissolved in 20 c.c. of dried carbon disulphide were then added slowly through the tap-funnel, the solution of bromine being shaken continuously during the process, and the operation being carried out in a darkened room. Colourless crystals were soon deposited in the bottle, and hydrogen bromide escaped through the calcium chloride tube. After remaining 12 hours in the dark, the solution was decanted, and the crystals washed with light petroleum; the crude material obtained in this way amounted to 4·5 grams, a further quantity being obtained from the mother liquor. The freshly precipitated substance melted at 178°. It was recrystallised from hot ethyl acetate, in which it dissolves readily, being deposited in aggregates of small, hard needles, which melt to a colourless liquid, evolving gas, at 182°; the melting point is dependent on the rate at which the temperature rises, and has been observed as high as 187°.

0·2164 gave 0·2174 CO_2 and 0·0649 H_2O. C = 27·40; H = 3·33.
0·1725 „ 0·2465 AgBr. Br = 60·80.
$C_9H_{13}O_2Br_3$ requires C = 27·48; H = 3·33; Br = 61·07 per cent.

The operation just described has been repeated many times, and the same result was obtained in each case. Even when the halogen solution was cooled by a freezing mixture, and the acid added as slowly as possible, in a dark room, hydrogen bromide was evolved after a very short interval, and crystals were deposited in the bottle when only a small proportion of the material had been added. Increasing the quantity of bromine does not improve the yield of the substance, which rarely exceeded 65 per cent. of the theoretical amount.

The tribromide of infracampholenic acid dissolves readily in alcohol, and the cold solution immediately develops with silver nitrate a turbidity which rapidly intensifies to a copious precipitate. It dissolves in aqueous sodium carbonate with liberation of carbon dioxide, forming a bromohydrocarbon and an unsaturated acid; if the alkali is added in small quantities amounting in all to one molecular proportion only, nearly two-thirds of the substance remains unchanged. The following experiment was therefore performed.

Twenty grams of the finely powdered tribromide were suspended in water, and treated with a cold solution of 21 grams (4 mols.) of anhydrous sodium carbonate. The substance dissolved almost immediately without liberating carbon dioxide, as this was absorbed by the excess of alkali. The turbid solution, after 24 hours, had deposited a heavy, colourless oil, which was removed by means of ether, washed twice with water, and freed from ether on the water-bath; on passing a current of steam through the residue, a bromohydrocarbon was obtained having an agreeable odour.

0·1908 gave 0·1781 AgBr. Br = 39·71.
0·1818 „ 0·1702 AgBr. Br = 39·83.
$C_8H_{11}Br$ requires Br = 42·78 per cent.

It is probable that this substance does not represent the initial product arising from the tribromide by the elimination of carbon dioxide and hydrogen bromide according to the equation :

$$C_9H_{12}O_2Br_3Na = C_8H_{11}Br + NaBr + HBr + CO_2.$$

Most likely the hydrocarbon dibromide, $C_8H_{12}Br_2$, is first produced, and undergoes resolution into the bromo-derivative, $C_8H_{11}Br$, and hydrogen bromide during the process of isolation, because the substance extracted by ether is colourless, becoming pale yellow when distilled in steam ; the aqueous residue in the distilling flask contains a considerable amount of hydrobromic acid, and holds some dark brown, non-volatile, tarry matter in suspension.

It will be interesting to ascertain the nature of the acid produced along with the hydrocarbon, and steps are being taken in this direction, but unfortunately the substance is resinous, and the only information concerning it which has been gained so far is the fact that it is unsaturated and contains bromine.

Dibromodihydroinfracampholenic acid, $C_9H_{14}O_2Br_2$.

Four grams of infracampholenic acid were dissolved in 100 c.c. of dry chloroform, and to the solution, immersed in a good freezing mixture, rather less than 4 grams of bromine, dissolved in 50 c.c. of cold chloroform, were slowly added. Owing to the readiness with which one atom of hydrogen in infracampholenic acid is replaced by bromine, great care was taken to keep the solution in a state of agitation, and the solution of bromine was admitted drop by drop; liberation of hydrogen bromide was thus reduced to a minimum, and only towards the end of the operation did the gas make its appearance. Without removing the vessel from the freezing mixture, a current of dry air was aspirated through the pale yellow liquid during one hour, after which interval the solution was allowed to acquire the temperature of the atmosphere. When the chloroform had completely evaporated, a white, butter-like mass remained; this was drained on porous earthenware, and washed several times with cold petroleum. The snow-white, micro-crystalline powder obtained in this way melts at 117° to a colourless liquid evolving gas; it dissolves very readily in alcohol and in cold ethyl acetate, but is rather sparingly soluble in boiling petroleum, which deposits it in minute rectangular plates; these melt and evolve gas at 125°.

0·2152 gave 0·2653 CO_2 and 0·0853 H_2O. C = 33·62 ; H = 4·40.
0·1599 „ 0·1940 AgBr. Br = 51·62.
$C_9H_{14}O_2Br_2$ requires C = 34·14 ; H = 4·46 ; Br = 50·95 per cent.

The dibromide dissolves immediately in aqueous sodium carbonate, and the turbid solution deposits a bromohydrocarbon on standing.

The Amide of Infracampholenic Acid.

When the extraordinary indifference of infracampholenamide towards alkaline hydrolytic agents was first observed, an attempt was made to study the oxidation products of the acid by oxidising the amide and hydrolysing the product.

Oxidation of Infracampholenamide.—Ten grams of the amide were dissolved in 5000 c.c. of boiling water and rapidly cooled, the temperature of the solution being finally reduced to about 0° by immersion in melting ice. Three hundred c.c. of a 2 per cent. solution of potassium permanganate were added in small quantities, the colour of the solution being immediately destroyed. The liquid was then treated with 15 grams of potassium carbonate, boiled, filtered, and evaporated to small bulk, when a dark yellow oil separated, and solidified on cooling. After being drained on porous earthenware, washed with a small quantity of cold water, and again drained, the colourless product weighed 8·5 grams.

Under these conditions, the amide is oxidised to a dihydroxy-derivative. The substance dissolves very readily in water, forming a solution which is neutral to litmus. Alcohol also dissolves it freely, and ethyl acetate is the most convenient solvent from which to crystallise it, depositing the derivative in prisms containing $1H_2O$. A specimen dried in the desiccator was analysed, with the following result :

0·1775 gave 0·3492 CO_2 and 0·1534 H_2O. C = 53·65 ; H = 9·60.
$C_9H_{17}O_3N,H_2O$ requires C = 52·68 ; H = 9·27 per cent.

In the hydrated condition the substance has no definite melting point, but liquefies at about 110°, when water is liberated. If the crystals deposited by ethyl acetate are powdered finely and dried at 90° until no further loss of water takes place, the substance melts at 170°, without evolving gas.

0·1816 gave 0·3861 CO_2 and 0·1500 H_2O. C = 57·99 ; H = 9·17.
0·2073 „ 0·4415 CO_2 „ 0·1694 H_2O. C = 58·08 ; H = 9·08.
0·2218 „ 14·2 c.c. of nitrogen at 16·5° and 779 mm. N = 7·63.
$C_9H_{17}O_3N$ requires C = 57·75 ; H = 9·09 ; N = 7·48 per cent.

The oxidised amide is hydrolysed by alcoholic potash much more

readily than infracampholenamide, but the acid obtained in this way takes the form of a resin.

Hydrobromide of Infracampholenamide, $C_9H_{16}ONBr$.—The amide of infracampholenic acid was dissolved in 48 per cent. hydrobromic acid, and allowed to remain in the desiccator. After some days, clusters of flat, transparent, rhomboidal plates separated. Cold alcohol dissolves the substance very readily, and it is also soluble in cold water, forming an acid solution; when potassium permanganate is added to this liquid, the colour is destroyed and bromine set free. The hydrobromide is insoluble in petroleum, and very sparingly soluble in cold ethyl acetate, but it dissolves readily in the boiling liquid, which deposits it in transparent plates melting at 144°, with vigorous disengagement of gas.

0·2165 gave 0·1603 AgBr. Br = 31·50.

$C_9H_{16}ONBr$ requires Br = 34·18 per cent.

$C_9H_{16}ONBr,H_2O$ „ Br = 31·74 „

An attempt to prepare the hydrobromide by dissolving the amide in more concentrated acid (sp. gr. 1·83) resulted in the production of *iso*lauronolamide. The clear solution in the acid deposited lustrous, colourless crystals melting indefinitely between 70° and 80°, and yielding *iso*lauronolamide and hydrobromic acid on treatment with water, which first converts the crystals into an oil; *iso*lauronolamide itself yields similar crystals under the influence of the concentrated acid, the product consisting most likely of an unstable salt.

Dibromide of Infracampholenamide, $C_9H_{15}ONBr_2$.—Ten grams of the amide were dissolved in dried chloroform, cooled in a freezing mixture, and treated with 10 grams of bromine (1 mol.) in the same solvent, the halogen being added in small quantities at a time; the bromine was immediately decolorised, and no hydrogen bromide was liberated. On evaporating the chloroform, colourless crystals were deposited, and the product was filtered from a small quantity of oil, washed with chloroform, and recrystallised from boiling ethyl acetate, which deposited it in white needles melting at 114°.

0·2148 gave 0·2435 AgBr. Br = 48·33.

0·2660 „ 0·3017 AgBr. Br = 48·26.

0·3321 „ 13·1 c.c. of nitrogen at 20° and 762 mm. N = 4·47.

$C_9H_{15}ONBr_2$ requires Br = 51·12; N = 4·60 per cent.

$C_9H_{15}ONBr_2,H_2O$ „ Br = 48·34; N = 4·23 „

The dibromide is insoluble in petroleum, but dissolves readily in alcohol, and is very freely soluble in water, forming a neutral solution from which it crystallises in white prisms; the aqueous liquid precipitates silver bromide from the nitrate, but does not liberate iodine

from potassium iodide, even when acidified with dilute sulphuric acid. It is indifferent towards a neutral solution of potassium permanganate, but in presence of dilute sulphuric acid bromine is liberated, and the permanganate decolorised.

Aminoinfracampholene, $C_8H_{13}\cdot NH_2$.

Ten grams of purified infracampholenamide were finely powdered and suspended in 25 c.c. of water; 10 grams of bromine were then dissolved in 100 c.c. of water containing 10 grams of caustic soda, and added to the amide. On gently warming the liquid, a basic odour became perceptible in a few minutes, and an oil rose to the surface. After about an hour, during which period the liquid was agitated, and at intervals gently heated, the base was extracted with ether, washed several times with water, and after removing the ether on a water-bath, distilled in an atmosphere of steam. The colourless oil obtained in this manner was collected by ether, dried with solid potash, and freed from ether on the water-bath. The yield amounted to 4 grams, and might possibly be augmented by manipulating smaller quantities of the amide at one time, because an experiment in which 25 grams of material were employed yielded only 9 grams of base.

Aminoinfracampholene is a colourless, limpid oil having a pungent, somewhat pleasant odour, and boils at 158—160° under 754 mm. pressure; it has a sp. gr. 0·8770 at 14°, and refractive index μ_{Na} 1·4748 at 19°. The base absorbs carbon dioxide readily from the air, forming a crystalline carbonate.

The *hydrochloride* is readily soluble in cold water, and crystallises in lustrous leaflets melting at 213°.

The *platinichloride* separates immediately in pale red crystals on adding aqueous platinic chloride to a solution of the hydrochloride in water. It dissolves very freely in hot alcohol, and crystallises in beautiful, lustrous, pale red leaflets.

0·1528 gave 0·0450 Pt. Pt = 29·45.

$(C_8H_{15}N)_2,H_2PtCl_6$ requires Pt = 29·48 per cent.

The salt darkens at about 200°, and melts to a charred mass at 238—240°.

The *picrate* crystallises in clusters of sulphur-yellow needles on adding to the base a hot solution of picric acid in alcohol.

0·2452 gave 33·8 c.c. of nitrogen at 18° and 752 mm. N = 15·75.

$C_8H_{15}N,C_6H_3O_7N_3$ requires N = 15·82 per cent.

It melts at 213° to a deep brown liquid which soon begins to evolve gas.

The *benzoyl* derivative is very readily soluble in ethyl acetate

and in alcohol, crystallising from the latter in rosettes of long, slender prisms melting at 105°; it is sparingly soluble in boiling petroleum, from which it separates in lustrous, silky needles which melt also at 105°.

0·1672 gave 0·4631 CO_2 and 0·1225 H_2O. C = 75·54; H = 8·14.
$C_{15}H_{19}ON$ requires C = 75·31; H = 7·95 per cent.

The *carbamide* derivative is not precipitated immediately on mixing moderately concentrated solutions of the hydrochloride and potassium cyanate, but soon crystallises when the liquid is heated on the water-bath; it forms lustrous, white needles melting at 182°.

0·1658 gave 24·5 c.c. of nitrogen at 17·5° and 756 mm. N = 17·01.
$C_9H_{16}ON_2$ requires N = 16·66 per cent.

The *phenylcarbamide* derivative separates in aggregates of flat, lustrous needles on adding a solution of phenylcarbimide in a mixture of ether with petroleum to a solution of the base (1 mol.) in ether.

0·1831 gave 0·4920 CO_2 and 0·1357 H_2O. C = 73·28; H = 8·23.
$C_{15}H_{20}ON_2$ requires C = 73·77; H = 8·19 per cent.

The substance crystallises from alcohol in very long, flat, transparent needles and melts at 180°.

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XI.—*Tutu. Part I. Tutin and Coriamyrtin.*

By THOMAS HILL EASTERFIELD, Professor of Chemistry, Victoria College, Wellington, N.Z., and BERNARD CRACROFT ASTON, Chemist to the New Zealand Department of Agriculture.

THE monotypic natural order, *Coriariæ*, is represented in New Zealand by three species, which are known collectively as Tutu or toot. *Coriaria ruscifolia*, L. (*C. Sarmentosa*, Forst; *C. arborea*, and *C. Tutu*, Lindsay; Tutu, pohou, and tupakihi of the Maori) is commonly known as the tree-toot; it is a handsome shrub with glossy, acuminate leaves, and grows to a height of 20—25 feet. *C. thymifolia*, Humb. and Bonp. (Tutu-papa or tutu-heu-heu of the Maori), seldom exceeds three feet in height, and is known as the ground-toot. *C. angustissima*, Hook. f., is of comparatively rare occurrence. It is a small, herbaceous upland annual with a characteristic fern-like appearance.

A peculiar interest attaches to these plants in that they are all known to be highly toxic. The animals brought by Captain Cook in both his voyages died in what was to him an unaccountable manner, but as Lauder Lindsay (*B. and F. Med. and Chir. Rev.*, July, 1865, 153; October, 1868, 465; also B.A. Report, 1862, 98) has pointed out, the general description of the symptoms leaves little doubt that they died of tutu poisoning. Many instances are upon record in which upwards of 50 per cent. of a large herd of cattle has been lost in a single night from toot poisoning. The plants are very succulent and attractive to cattle, so that stock can only be driven through a tutu country at considerable risk. Cattle living in these districts appear to eat the plant with impunity, but if starved or overdriven, the apparent toleration disappears, partly, no doubt, from the fact that under these circumstances the plant is eaten in excessive quantity.

Cattle suffering from tutu poison, popularly said to be tooted, rush madly about, then stagger and fall, convulsions are of frequent occurrence, large volumes of gas appear in the stomach, and the animal eventually dies in a comatose condition. Tutu berries are of luscious appearance and taste, and are consumed in quantity by the Maoris; the seeds are, however, poisonous, and deaths from swallowing them are not uncommon, particularly amongst children. It is said that birds are not poisoned by the seeds, but cases have come under the notice of the authors in which domestic fowls have been poisoned by eating the berries, the symptoms being typical of tutu poisoning. Human beings who have recovered from toot poisoning nearly always suffer for a time from impaired memory, and permanent physical distortion sometimes accompanies severe cases. Bleeding is the usual remedy adopted by the natives and settlers, and the beneficial effect is remarkably rapid.

It is somewhat remarkable that the poisonous constituent of tutu has remained hitherto unisolated. Skey (*Trans. N.Z. Inst.*, 1869, 153, 399, 400) has shown that ether removes from the seeds a highly poisonous green oil, which, he remarks, is or contains the poison. Hughes (*Trans. N.Z. Inst.*, 1870, 237) showed that *C. rusci-folia* contained crystalline constituents soluble in alcohol or water, but did not identify them. He found that boiling with slaked lime destroyed the poisonous action of the drug. Christie (*N.Z. Med. Journ.*, July and October, 1890) has examined the physiological effect of decoctions of the plant, and denies that lime destroys the poison.

The present paper contains an account of the investigation of the three species of New Zealand *Coriaria*. It is shown that the plants all contain a highly poisonous, non-nitrogenous glucoside, $C_{17}H_{20}O_7$, for which the name tutin is proposed. *C. thymifolia* also contains quercetin

and some half-dozen well-known acids, and *C. angustissima* has yielded a volatile acid, $C_8H_8O_4$, which has not been identified.

Experimental.

(1). *Coriaria thymifolia.*—Eleven kilograms of the air-dried plant (root excluded) gathered at Dunedin at the time of flowering (January) were put through a chaff-cutter and boiled with successive quantities of water. The concentrated infusion was treated with a large volume of alcohol which precipitated inorganic salts, ellagic acid, and a large quantity of black, tarry matter. The residue remaining after distilling off the alcohol from the supernatant liquid was extracted with ether. When the ether was distilled off, the residue containing the characteristic glucoside tutin set to a semi-solid, crystalline mass with a pungent odour.

Acetic acid was recognised by distilling the mass with steam. From the distillate a silver salt was prepared, which, after a single recrystallisation, gave Ag = 64·3 per cent. Calculated for $C_2H_3O_2Ag$, Ag = 64·7 per cent.

Gallic acid remained in quantity when the solution, which had been distilled with steam, was evaporated to the crystallising point and the residue extracted with chloroform. It gave the usual colour reactions. After recrystallisation from water, it was dried at 150° and gave:

C = 49·4; H = 3·5 per cent.

$C_7H_6O_5$ requires C = 49·0; H = 3·5 per cent.

Quercetin, or some isomeric compound, was present in the crude gallic acid. After purification by repeated recrystallisation from water, it showed the usual colour reactions and dyeing properties, lost 2 mols. of water at 160°, and, on analysis, gave:

C = 59·2; H = 3·6 per cent.

$C_{15}H_{10}O_7$ requires C = 59·6; H = 3·2 per cent.

Quercetin has been definitely shown by Perkin to exist in *C. myrtifolia* (Trans., 1900, **77**, 429).

The chloroform solution separated from the gallic acid was evaporated and the product dissolved in ether, the remaining acids were then removed by sodium carbonate.

Succinic acid was identified in the alkaline solution. It was recognised by qualitative reactions, melting point, and analysis of the silver salt.

C = 14·3; H = 1·25; Ag = 64·8 per cent.

$C_4H_4O_4Ag_2$ requires C = 14·4; H = 1·2; Ag = 65·0 per cent.

Seeds.—A kilogram and a half of the seeds of *C. thymifolia* were pul-

verised and exhausted by carbon disulphide which removed 22·6 per cent. of a green, drying oil. The seeds, freed from oil, yielded to water a small quantity of tutin which was extracted with ether, and after recrystallisation melted at 208—209°. The oil upon saponification yielded a liquid acid which was probably linoleic acid, since its calcium and barium salts were readily soluble in ether.

(2). *C. ruscifolia.*—In the examination of this plant, the juice expressed from the succulent, asparagus-like shoots (gathered at Wellington early in October) was employed. It contained the same acids as the extracts of *C. thymifolia.* The yield of tutin was 0·03 per cent. Samples of the plant gathered later in the year from the same hill-side, contained a smaller percentage of the poison. The dried seeds of *C. ruscifolia,* on extraction with carbon disulphide, yielded 22·8 per cent. of oil which was very faintly toxic. 0·18 gram administered to a small kitten produced only very mild symptoms of tutu poisoning. From the extracted seeds, water removed a few crystals of a substance which gave the characteristic bitter taste and colour reaction of tutin.

(3). *C. angustissima.*—Only 1 kilogram of the dried plant was obtainable. It was collected at Dunedin early in January. Tutin was obtained from it and identified by its melting point. This species contains an acid which was not detected in the other two; when the aqueous extract of the plant was repeatedly shaken up with ether, the later extractions contained the acid in a comparatively pure condition. It crystallised from chloroform in silky, yellowish needles which were finally sublimed at 125° under diminished pressure. It was thus obtained in colourless, iridescent plates, very readily soluble in water, alcohol, or ether. The acid has a characteristic smell, gives a transient violet colour with ferric chloride, and melts at 130° (uncorr.). On analysis:

0·1214 gave 0·2537 CO_2 and 0·0545 H_2O. C = 56·99; H = 4·99.
$C_8H_8O_4$ requires C = 57·10; H = 4·76 per cent.

Tutin.

The ethereal solution, from which all the acids had been removed, was evaporated and yielded almost colourless crystals which were repeatedly recrystallised from water and from alcohol. From water, the substance separates in characteristic acicular forms, from alcohol, in oblique ended prisms. The compound is perceptibly volatile, may be slowly sublimed at 120—130°, melts at 208—209° (uncorr.), and has an intensely bitter taste. It contains no nitrogen, and after hydrolysis by dilute acids reduces Fehling's solution, and with phenylhydrazine gives an amorphous precipitate which is not phenylglucosazone.

Strong sulphuric acid added to a few drops of a saturated aqueous solution of tutin gives a blood-red coloration.

Examination by Zeisel's method for methoxyl groups gave negative results. When evaporated to dryness with slaked lime, solutions of tutin yield amorphous compounds amongst which tutin can no longer be detected even when the residue has been acidified.

Some preliminary experiments upon the toxic effect of tutin were carried out by Mr. J. A. Gilruth, Chief Government Veterinary Surgeon. The compound is very poisonous. A dose of 0·129 gram killed a kitten weighing 1 kilogram in 40 minutes; 0·001 gram given to a cat weighing 2 kilograms caused a fit in 3 hours and illness for the next 24 hours. The same cat subsequently succumbed to a dose of 0·003 gram.

A dose of about a milligram produced nausea, vomiting, and incapacity for work extending over 24 hours in a healthy, full-grown man.

Three preparations were analysed, i and ii from *C. thymifolia* and iii from *C. ruscifolia*:

i. 0·1299, dried at 120—130°, gave 0·2899 CO_2 and 0·0691 H_2O. C = 60·78; H = 5·91.

ii. 0·1255, dried in desiccator, gave 0·2793 CO_2 and 0·0710 H_2O. C = 60·70; H = 6·20.

iii. 0·1264, dried at 120—130°, gave 0·2825 CO_2 and 0·0658 H_2O. C = 60·95; H = 5·78.

$C_{17}H_{20}O_7$ requires C = 60·71; H = 5·95 per cent.

Molecular Weight Determinations.—Calculated for $C_{17}H_{20}O_7$. M = 336.

0·403 gram	depressed the m. p. of	10 grams	of	acetic acid	0·47°. M = 332.
0·319 „	„	„	„	„	0·38°. M = 325.
0·2448 „	„	„ 8	„	phenol	0·66°. M = 333.
1·1173 grams	raised the b.p. of	11·65	„	alcohol	0·35°. M = 320.

Solubilities.—One hundred grams of water at 10°, of ether at 10°, and of alcohol at 16° dissolve 1·9, 1·5, and 8·2 grams of tutin respectively. It is very soluble in acetone, but dissolves only sparingly in chloroform, and is insoluble in benzene or carbon disulphide.

The optical activity has been determined by Professor C. R. Marshall, of University College, Dundee, who reports as follows:

$\alpha_D = +0·37°$; $l = 2$ dcm.; $d = 0·8$; $c = 2·5$ per cent. in alcohol; whence $[\alpha]_D^{19·5°} = +9·25$.

Note on the Pharmacology of Tutin.—Professor Marshall has undertaken the pharmacology of tutin, and furnishes the following preliminary note:

"Tutin, pharmacologically, is closely allied to coriamyrtin, and

belongs to what is known as the picrotoxin group of substances. After preliminary depression, it induces salivation, a fall in the frequency of the pulse, and increased respiratory activity, followed by convulsions, for the most part clonic and limited in the earlier stages to the fore part of the body. The effect is apparently due to an action on the medulla oblongata and basal ganglia of the brain.

"It differs from coriamyrtin in being less toxic and slower in its action. On this account, the preliminary depression is more marked. Its connection with this substance, however, is close. Experiments suggest that it is broken up in the body into some substance, possibly coriamyrtin, which is the active convulsant factor.

"It ought to be stated that the coriamyrtin employed by me was obtained from Merck. After boiling for a short time with dilute hydrochloric acid (2 per cent.), it did not reduce copper sulphate solution. It melted at 224° (uncorr.), and its solubility in physiological saline solution (0·6 per cent. NaCl) was less than 0·1 per cent. Riban's coriamyrtin melted at 220°, and was soluble in water to the extent of 1·44 per cent. at 22°."

Coriamyrtin.

The physiological action of the New Zealand species of *Coriaria* and of the European species (*C. myrtifolia*) is so similar that a direct comparison of tutin with coriamyrtin, the glucoside isolated by Riban (*Bull. Soc. Chim.*, 1864, [ii], 1, 87; 1867, [ii], 7, 79), seemed desirable. A gram of coriamyrtin was obtained from Merck, of Darmstadt; the specimen melted at 225° (uncorr.),* and the melting point was not altered by recrystallisation from alcohol. Like tutin, the compound is somewhat volatile, sublimation commencing at about 150°. Analysis of the compound before and after crystallisation gave numbers agreeing closely with those obtained by Riban:

0·1389 gave 0·3288 CO_2 and 0·0822 H_2O. C = 64·56; H = 6·57.
0·1263 „ 0·2976 CO_2 „ 0·0734 H_2O. C = 64·25; H = 6·45.
Riban found (mean of three analyses) C = 64·07; H = 6·57.
$C_{30}H_{36}O_{10}$ (Riban) requires C = 64·75; H = 6·47 per cent.
$C_{21}H_{26}O_7$ requires C = 64·61; H = 6·66 per cent.

If the latter formula were correct, coriamyrtin would differ from tutin by C_4H_6 only, and its higher melting point, lower volatility, and solubility suggest strongly that it is a higher member of the series to which tutin belongs. Molecular weight determinations, however, indicate that the true formula is smaller than either of the above, being probably half that assigned to tutin by Riban.

* Riban gives 220°; Merck (*Chem. Centr.*, 1899, i, 706) gives 229°.

0·2478 gram raised the b. p. of 3·76 grams of acetone 0·46°. M = 255.
0·3196 „ „ 6·4 „ „ 0·33°. M = 265.
0·1732 „ depressed the m. p. of 8 „ phenol 0·62°. M = 250.
0·2226 „ „ „ 8 „ „ 0·80°. M = 250.

Calculated for $C_{15}H_{18}O_5$, M = 278; and for $C_{21}H_{26}O_7$, M = 390.

The conclusion that the real formula is $C_{15}H_{18}O_4$ harmonises with the fact that, by the action of bromine, Riban obtained a crystalline derivative in which 1/18th of the hydrogen was replaced by the halogen. If, however, the compound is a glucoside, as its reactions suggest, the sugar which it yields upon hydrolysis cannot contain more than four atoms of oxygen, and the formula is remarkable in that it contains fewer oxygen atoms than that of any glucoside hitherto described.

The appended table shows the chief differences between tutin and coriamyrtin:

	Tutin, $C_{17}H_{20}O_7$.	Coriamyrtin, $C_{15}H_{18}O_5$ (E. and A.).
Solubility in 100 parts of water...	1·8 at 10°	1·44 at 22° (Riban)
Solubility in 100 parts of alcohol..	8·2 at 16°	2·00 at 22° „
Reaction with hydriodic acid, followed by potash	Nil.	Magenta* „
With concentrated sulphuric acid..	Blood red	Dirty yellow
Initial temperature of sublimation	About 120°	About 150°

The authors desire, in conclusion, to express their thanks to Mr. J. D. Ritchie, and the other officers of the New Zealand Department of Agriculture, for their kindness in securing the raw material employed n this investigation of tutu.

XII.—*Some α-Alkyl Substitution Products of Glutaric, Adipic, and Pimelic Acids.*

By J. W. Mellor.

The α-alkyl substitution products of glutaric, adipic, and pimelic acids have been comparatively little studied, and, as it was thought that it would be interesting to prepare some of these derivatives and determine their dissociation constants, I undertook the following work at the suggestion of Professor W. H. Perkin, jun.

The α-methyl- and α-ethyl-glutaric acids have been prepared by Auwers and Titherly (*Annalen*, 1896, **292**, 209—213).

In preparing derivatives of adipic acid, I have employed a modification

* Reaction verified by the authors.

of the process described by Montemartini (*Ber.*, 1895, 28, 985). Montemartini first prepared ethyl butanetricarboxylate by the interaction of the sodium compound of ethyl malonate with ethyl γ-chlorobutyrate :

$$(CO_2Et)_2CHNa + CH_2Cl\cdot CH_2\cdot CH_2\cdot CO_2Et = (CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2Et + NaCl.$$

This ester, by hydrolysis and subsequent decomposition of the resulting tricarboxylic acid by heat, yields adipic acid. Montemartini also showed that α-substituted derivatives of adipic acid may be obtained by using homologues of ethyl malonate in this synthesis, and in this way he prepared α-methyl- and α-ethyl-adipic acids.

Since, however, the ethyl γ-chlorobutyrate required for these experiments had to be prepared by the hydrolysis of γ-chlorobutyronitrile, $CH_2Cl\cdot CH_2\cdot CH_2\cdot CN$, by a troublesome operation conducted in sealed tubes, I have simplified the process by carrying out the synthesis with the nitrile instead of with the ester. The preparation of adipic acid, for example, may be readily accomplished as follows:

The sodium compound of ethyl malonate is treated with γ-chlorobutyronitrile, when the following decomposition takes place :

$$(CO_2Et)_2CHNa + CH_2Cl\cdot CH_2\cdot CH_2\cdot CN = NaCl + (CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN.$$

It is now only necessary to boil the ethyl ω-cyanobutane-αα-dicarboxylate thus formed with dilute sulphuric acid, when hydrolysis and elimination of carbon dioxide simultaneously occur, and adipic acid is formed.

If instead of ethyl malonate the substitution products of ethyl malonate are employed in the above synthesis, it is an easy matter to prepare any α-substitution product of adipic acid. However, in the examples given in the paper, the γ-chlorobutyronitrile was converted into ethyl γ-chlorobutyrate, $CH_2Cl\cdot CH_2\cdot CH_2\cdot CO_2Et$, and this was digested with the sodium compound of the ethyl alkylmalonate. The ester thus obtained gave, on hydrolysis, the desired substituted acid, with elimination of carbon dioxide. The simplification in the process above-mentioned was suggested to me by Professor Perkin after the three alkyl-adipic acids had been prepared.

In the preparation of the substituted pimelic acids, the process employed was essentially that of Crossley and Perkin (Trans., 1894, 65, 989). The sodium compound of a substitution product of ethyl malonate is first treated with trimethylene chlorobromide, when the following reaction takes place :

$$(CO_2Et)_2CRNa + CH_2Br\cdot CH_2\cdot CH_2Cl = (CO_2Et)_2CR\cdot CH_2\cdot CH_2\cdot CH_2Cl + NaBr.$$

The chloro-ester so prepared is then allowed to react with the sodium compound of ethyl malonate, thus:

$$(CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CH_2Cl + NaCH(CO_2Et)_2 = (CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2 + NaCl.$$

The tetracarboxylic ester so produced is digested with hydrochloric acid, when hydrolysis and elimination of carbon dioxide takes place, and the α-substituted pimelic acid is prepared.

α-Alkyl-glutaric Acids.

α-Methylglutaric Acid, $CO_2H\cdot CH(CH_3)\cdot CH_2\cdot CH_2\cdot CO_2H$.—In preparing this acid, sodium (1 at.) is dissolved in absolute alcohol and mixed with ethyl propanetricarboxylate, $(CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CO_2Et$ (1 mol.). A slight excess of methyl iodide (1 mol.) is then added, and after heating for 2 hours on the water-bath, the product is diluted with water and the oily ester extracted with ether in the usual way. After drying over calcium chloride and fractionation, the ethyl methylpropanetricarboxylate, $(CO_2Et)_2\cdot C(CH_3)\cdot CH_2\cdot CH_2\cdot CO_2Et$, which distils at 165° under 20 mm. pressure, is digested with concentrated hydrochloric acid for about 6 hours. After evaporation to dryness, a viscid mass remains which soon solidifies. The product crystallises from water in a vacuum, melts at 77—78°, and consists of pure α-methylglutaric acid.

This acid has been prepared in a variety of ways, but the above appears to be the best method.

The dissociation constants were as follows:

v.	μ_v	*m.*	*K.*
85	22·66	0·0642	0·0052
170	32·23	0·0913	54
340	45·18	0·1280	55
680	61·42	0·1740	54

Temp. 24·4°; $\mu_\infty = 352$; $K = 0·0054$.

Bethmann (*vide infra*) gives 0·0054; Walden (*vide infra*) 0·0052.

α-Ethylglutaric Acid, $CO_2H\cdot CH(C_2H_5)\cdot CH_2\cdot CH_2\cdot CO_2H$.—This acid has lately been prepared by Auwers and Titherly (*loc. cit.*) by the hydrolysis of ethyl α-ethylpropanetricarboxylate,

$$(CO_2Et)_2\cdot C(C_2H_5)\cdot CH_2\cdot CH_2\cdot CO_2Et.$$

I used the same process, and found the boiling point of this ester to be 175—179° (30 mm.), and the melting point of the acid to be 60—61° (Auwers and Titherly give 60·5°).

The dissociation constants were as follows:

v.	μ_v.	m.	K.
44·6	16·86	0·0479	0·0054
89·2	23·99	0·0685	56
178·2	34·04	0·0967	58
356·8	47·03	0·1336	57
713·6	63·18	0·1795	55

Temp. 24·2°; $\mu_\infty = 352$; $K = 0·0056$.

Pfaff (*Annalen*, 1896, **292**, 214) gives $K = 0·0058$.

α-Propylglutaric Acid, $CH_3·CH_2·CH_2·CH(CO_2H)·CH_2·CH_2·CO_2H$.—This acid, which does not appear to have been previously described, was obtained in a similar way to the α-ethyl acid just mentioned.

Ethyl α-propylpropanetricarboxylate,

$$(CO_2Et)_2C(C_3H_7)·CH_2·CH_2·CO_2Et,$$

was first prepared by treating the sodium compound of ethyl propanetricarboxylate with propyl iodide, and the ester, which distils at 180—185° under 32 mm. pressure, was hydrolysed by boiling with hydrochloric acid. α-Propylglutaric acid crystallises by evaporation of the aqueous solution in a vacuum, and melts at 66—68°. On analysis:

0·1093 gave 0·2234 CO_2 and 0·0826 H_2O. C = 55·7; H = 8·4.

$C_8H_{14}O_4$ requires C = 55·2; H = 8·1 per cent.

The dissociation constants were as follows:

v.	μ_v.	m.	K.
62·54	20·20	0·0575	0·0058
125·08	28·67	0·0116	58
250·16	40·75	0·1161	61
500·32	55·36	0·1577	59
1000·64	76·07	0·2167	59

Temp. 24·4°; $\mu_\infty = 35$; $K = 0·00586$.

α-Isopropylglutaric Acid, $(CH_3)_2CH·CH(CO_2H)·CH_2·CH_2·CO_2H$.—The acid employed in the following determination was the specimen prepared by Perkin (Trans., 1896, **69**, 1495). It melted at 94°.

The dissociation constants were as follows:

v.	μ_v.	m.	K.
36·5	15·30	0·0436	0·00548
73	21·85	0·0623	567
146	30·19	0·0860	555
292	41·59	0·1185	541
584	57·88	0·1649	559
1168	79·25	0·2258	563

Temp., 24·4°; $\mu_\infty = 351$; $K = 0·00555$.

Adipic Acid and the α-Alkyl-adipic Acids.

Adipic Acid, $CO_2H \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$.—According to Markownikoff (*Annalen*, 1898, **302**, 34) and Aschan (*Ber.*, 1899, **32**, 1771), adipic acid is readily prepared by the oxidation of Russian light petroleum, boiling at 80—82°, with nitric acid, but it is difficult to obtain Russian light petroleum in this country. The next best way of preparing adipic acid appears to be the following.

Trimethylene chlorobromide, $CH_2Cl \cdot CH_2 \cdot CH_2Br$, is treated with potassium cyanide, and the product converted into γ-chlorobutyronitrile, $CH_2Cl \cdot CH_2 \cdot CH_2 \cdot CN$, as described by Gabriel (*Ber.*, 1890, **23**, 1771; compare Henry, *Compt. rend.*, 1885, **101**, 358). This nitrile is then digested with the calculated quantity of the sodium compound of ethyl malonate in the usual way, and the *ethyl cyanopropylmalonate*, $CN \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(CO_2Et)_2$, boiling between 170° and 175° under 40 mm. pressure, thus obtained is boiled with dilute sulphuric acid (1 : 2) for 5 hours, and the adipic acid produced is extracted with ether, and purified by recrystallising once from water. This process not only gives a good yield, but the acid is at once obtained in a state of purity.

α-Methyladipic Acid, $CO_2H \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$.—This acid was first prepared by Bone and Perkin (Trans., 1895, **65**, 115), and subsequently by Montemartini (*Gazz.*, 1896, **26**, ii, 278).

The acid used in the following determinations was prepared in the following way.

Ethyl γ-chlorobutyrate, obtained from γ-chlorobutyronitrile by the method described by Henry (*Bull. Soc. Chim.*, 1885, [ii], **45**, 341), was digested with the calculated quantity of the sodium compound of ethyl methylmalonate for 2 hours. After adding water and extracting with ether, an oil was obtained which distilled constantly at 175—178° under 33 mm. pressure, and evidently consisted of ethyl α-methylbutanetricarboxylate. This, on hydrolysis with concentrated hydrochloric acid, yielded α-methyladipic acid melting at 63° (Perkin and Bone give the melting point as 64°).

The dissociation constants were as follows:

v.	μ_v.	m.	k.
54·31	15·84	0·0450	0·0039
108·62	22·46	0·0638	40
217·24	31·72	0·0901	41
434·48	44·86	0·1275	43
868·96	62·56	0·1780	44

Temp. 24·4°; $\mu_\infty = 352$; $K = 0{\cdot}0041$.

α-Ethyladipic Acid, $CO_2H \cdot CH(C_2H_5) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$.—This

acid has already been obtained by Lean and Lees (Trans., 1897, 71, 1067), and by Montemartini (*Ber.*, 1896, 29, 1115).

The specimen used in the following experiments was prepared from ethyl α-ethylbutanetricarboxylate, $(CO_2Et)_2C(C_2H_5)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2Et$, boiling at 180—183° under 28 mm. pressure, by hydrolysis with boiling hydrochloric acid and elimination of carbon dioxide. α-Ethyladipic acid melts at 48°.

The dissociation constants were as follows:

v.	μ_v.	*m.*	*k.*
47·2	15·08	0·0429	0·0041
94·4	20·66	0·0589	39
188·8	30·20	0·0866	43
377·6	40·63	0·1158	40
755·2	57·57	0·1640	43

Temp. 24·2°; $\mu_\infty = 351$; $K = 0{\cdot}00415$.

α-Propyladipic Acid, $CO_2H\cdot CH(C_3H_7)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$.—This acid, which has not been previously described, was prepared in a similar way to the corresponding α-ethyl acid, namely, by the hydrolysis of *ethyl α-propylbutanetricarboxylate* and elimination of carbon dioxide. The last-named ester boils at 200—205° under 30 mm. pressure. The acid, which melted not quite sharply at 55—59°, was analysed with the following results:

0·1293 gave 0·2736 CO_2 and 0·1005 H_2O. C = 57·6; H = 8·6.

$C_9H_{16}O_4$ requires C = 57·4; H = 8·5 per cent.

The dissociation constants were as follows:

v.	μ_v.	*m.*	*K.*
38·51	13·31	0·0380	0·0039
77·02	19·12	0·0546	41
154·04	27·35	0·0810	43
305·08	38·07	0·1088	43
601·16	52·53	0·1501	43

Temp. 24·4°; $\mu_\infty = 350$; $K = 0{\cdot}0042$.

α-Alkyl-pimelic Acids.

α-Methylpimelic Acid, $CO_2H\cdot CH(CH_3)\cdot[CH_2]_3\cdot CH_2\cdot CO_2H$.—This acid has already been prepared by Zelinsky and Generowsow (*Ber.*, 1896, 29, 729), and by Einhorn (*Annalen*, 1897, 295, 175). It melts at 57—58°. The determinations of the dissociation constant by Zelinsky and Generowsow gave the value $K = 0{\cdot}00315$.

α-Ethylpimelic Acid, $CO_2H\cdot CH(C_2H_5)\cdot[CH_2]_3\cdot CH_2\cdot CO_2H$.—This acid has already been obtained by Crossley and Perkin (*loc. cit.*), and is described by them as an oil. I have somewhat modified their

method of preparation in the hope of obtaining the acid in a crystalline condition, but without success.

If 1 gram-molecule of trimethylene chlorobromide is treated with 1 gram-molecule of the sodium compound of ethyl malonate in the usual way, a 22 per cent. yield of ethyl ω-chloropropylethylmalonate is produced (Crossley and Perkin, *loc. cit.*, 991), distilling at 145° under 18 mm. pressure. When this chloro-ester is heated with a large excess of concentrated hydrochloric acid (sp. gr. 1·16) for 6 hours on a sand-bath, and the product extracted with ether in the usual way, δ-chlorovaleric acid, $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, is obtained as an oil. This, on esterification with alcohol and hydrogen chloride, yields *ethyl δ-chlorovalerate*, $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$, as a colourless oil, boiling at 120—125° under 40 mm. pressure. This ester was analysed with the following result:

0·1846 gave 0·1627 AgCl. Cl = 21·8.
$C_7H_{13}O_2Cl$ requires Cl = 21·5 per cent.

The chloro-ester was digested in alcoholic solution with the calculated quantity of the sodium compound of ethyl ethylmalonate, water was then added, and the oily product extracted with ether, the ethereal solution washed with water, dried over calcium chloride, and evaporated. The residual oil was purified by fractional distillation under reduced pressure. In this way, *ethyl ethylpentanetricarboxylate*, $(CO_2Et)_2C(C_2H_5){\cdot}[CH_2]_3{\cdot}CH_2{\cdot}CO_2Et$, was obtained as a colourless oil boiling at 189—191° under 20 mm. pressure. On analysis:

0·2055 gave 0·4528 CO_2 and 0·1658 H_2O. C = 60·1; H = 8·9.
$C_{16}H_{28}O_6$ requires C = 60·8; H = 8·8 per cent.

On hydrolysing this ester with hydrochloric acid in the usual way, α-ethylpimelic acid was obtained as a thick oil which even on standing for 3 months in a vacuum over sulphuric acid showed no signs of crystallisation.

No determinations of the dissociation constants were made, since the acid was not considered pure enough for the purpose.

The Dissociation Constants.

I have collected, in the table on p. 133, the known dissociation constants for the α-alkyl-succinic, -glutaric, -adipic, and -pimelic acids.

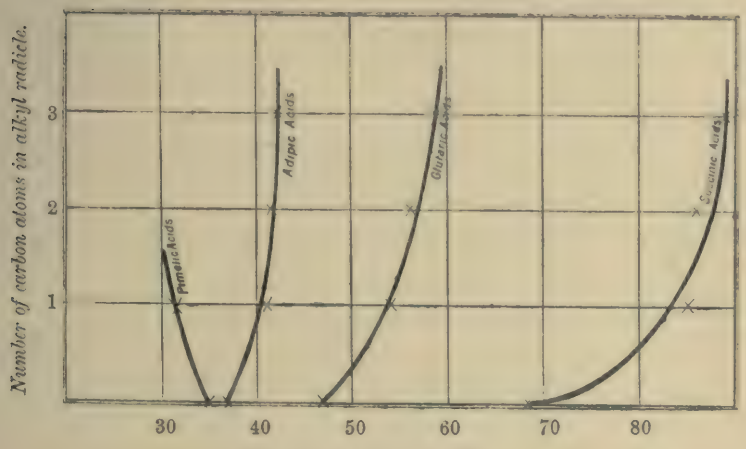
The numbers for the succinic acids are from Bethmann's (*Zeit. physikal. Chem.*, 1890, **5**, 413), and Walden's (*ibid.*, 1892, **8**, 433) papers, those for glutaric acid and adipic acid from Ostwald's paper (*ibid.*, 1889, **3**, 170, 241, 369). The value for pimelic acid is the mean of those prepared by different methods given in Walden's paper, and is

α-Alkyl radicle.	Succinic acid.	Glutaric acid.	Adipic acid.	Pimelic acid.
Parent acid	0·0068	0·0047	0·0037	0·0035
Methyl	0·0085	0·0054	0·0041	0·0031
Ethyl	0·0086	0·0056	0·00415	—
Propyl	0·0089	0·0059	0·00423	—
*iso*Propyl	0·0075	0·0055	—	—
*iso*Butyl	0·0088	—	—	—
Allyl	0·0109	—	—	—
(Benzoyl)	0·0091	—	—	—

identical for that of synthetical pimelic acid prepared by Perkin's process (Trans., 1887, 51, 241).

The chief point of interest lies in the fact that, although the avidity of succinic, glutaric, and adipic acids increases when hydrogen is replaced by an α-alkyl group, yet the effect with pimelic acid appears to be the converse of this. For example, the differences between the values of this constant for these acids and their respective α-methyl derivatives are as follows :—

Methylsuccinic acid—succinic acid	+0·0017
Methylglutaric acid—glutaric acid	+0·0007
Methyladipic acid—adipic acid	+0·0004
Methylpimelic acid—pimelic acid	−0·0004



The effect of the substitution thus appears to become less marked as the distance between the carboxyl groups increases. These facts may be shown graphically by plotting the number of carbon atoms

in the introduced methyl, ethyl, or propyl group, against the value of $K \times 10^4$.

The curves on page 133 indicate:

(1) The effect of the substitution is greater the heavier the alkyl group introduced.

(2) With succinic, adipic, and pimelic acids the effect of the substitution is less marked the further the carboxyl groups are apart, as is evident from the gradual flattening of the curves from succinic to adipic acid.

(3) The reversal in the direction of the slope of the curve in the case of pimelic acid and its methyl derivative seems to indicate that in the suberic, azelaic, and sebacic series a still greater reversal will be observed when the dissociation constants of the α-alkyl substitution products of these acids have been determined.

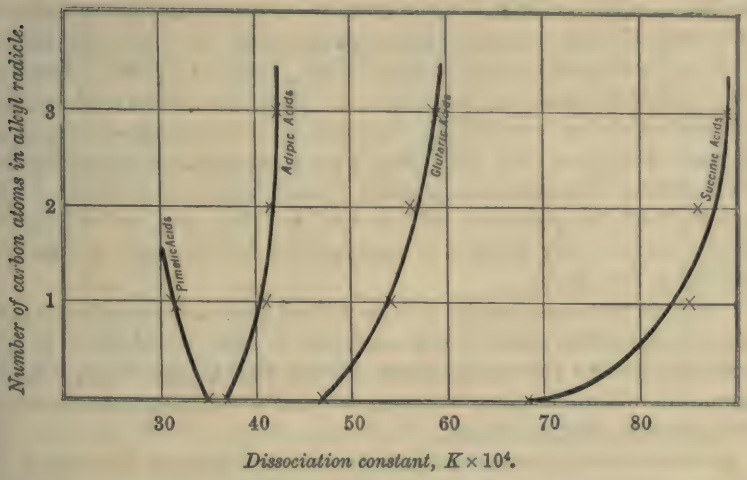
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Propyl	0·0089	0·0059	0·00423	—
*iso*Propyl	0·0075	0·0055	—	—
*iso*Butyl	0·0088	—	—	—
Allyl	0·0109	—	—	—
(Benzoyl)	0·0091	—	—	—

identical for that of synthetical pimelic acid prepared by Perkin's process (Trans., 1887, 51, 241).

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XIII.—*Santalenic Acid.*

By Alfred C. Chapman, F.I.C.

A few years ago, in conjunction with Mr. H. E. Burgess, I undertook an examination of the hydrocarbon obtained by distilling santalol with phosphoric oxide, chiefly for the purpose of comparing its properties with those of cedrene. In the preliminary note in which the results of this investigation were given (Proc., 1896, 12, 140), reference was incidentally made to the formation of a crystalline acid by the action of oxidising agents on oil of sandal-wood, for which we suggested the name *santalenic acid*. At that time circumstances compelled me to discontinue the work, but recently I have been able to make a further study of the properties of this acid and its salts, as well as of the conditions under which it is most readily formed, with the results detailed in this paper.

In my earlier experiments, that fraction of the sandal-wood oil which boiled at 301—306° (corr.) was used, but I soon found that it was much simpler and more economical to work with the oil itself. Of the samples of oil used, which were all of undoubted genuineness, three were specially distilled for me.

As the result of numerous experiments made with the object of ascertaining the conditions under which the best yield was obtained, the following procedure was finally adopted. To 20 c.c. of the oil in a large flask an aqueous solution of potassium permanganate containing 50 grams per litre is added in successive quantities of about 20 c.c.

at a time, the contents of the flask being thoroughly shaken after each addition. At first, the permanganate is rapidly reduced with the development of a considerable amount of heat, but when about two-thirds of the solution has been used the oxidation proceeds more slowly. After the whole has thus been added, and the reduction is complete, the oxides of manganese are filtered off, and the filtrate is acidified with sulphuric acid. The precipitated santalenic acid, after having been allowed to stand for a short time, is filtered off, thoroughly washed with cold water, and dried on a porous tile. Working in this manner, an average yield of 20 per cent. was obtained, but it was found that this depended to some extent on the origin of the oil used, as well as on the rate at which the oxidation was allowed to proceed.

The air-dried acid is then dissolved in alcohol, and water added until the point at which precipitation of the acid occurs is nearly reached. On allowing this solution to stand in a cool place for some hours, the santalenic acid crystallises out in large, transparent plates, and may be further purified by a second crystallisation. After drying in a vacuum over sulphuric acid, two different preparations were analysed, with the following results:

0·2010 gave 0·5540 CO_2 and 0·1695 H_2O. C = 75·17; H = 9·36.
0·2105 „ 0·5810 CO_2 „ 0·1800 H_2O. C = 75·28; H = 9·50.
$C_{13}H_{20}O_2$ requires C = 75·00; H = 9·61 per cent.

Titration of the Acid with Soda.—Sodium hydroxide (prepared from sodium) containing 0·00506 gram Na per c.c. was run into a solution of the acid in dilute alcohol, phenolphthalein being used as indicator.

0·494 gram of the acid required for neutralisation 11·4 c.c. of soda solution (= 0·0576 gram Na). For a monobasic acid of the formula $C_{13}H_{20}O_2$, 0·0546 gram Na would be required.

Molecular Weight.—Two determinations by the freezing point method, using acetic acid as solvent, gave the following results:

Weight of acid.	Weight of solvent.	Depression of freezing point.	Mol. weight.
0·185 gram.	8·807 grams.	0·419°	194
0·388 „	8·430 „	1·030°	173

These numbers are in fair accordance with the molecular weight corresponding with the formula $C_{13}H_{20}O_2$, namely, 208. Using benzene as a solvent, much higher numbers were obtained, but it is well known that many organic acids give abnormal results in benzene solution.

Santalenic acid crystallises in thin, colourless plates having a brilliant pearly lustre, is insoluble in water, but dissolves readily in all the ordinary organic solvents. It melts at 76°, boils without decomposition at 189° (corr.) under a pressure of 28 mm., and can be distilled

with steam. Santalenic acid is dextrorotatory. A determination of its specific rotatory power in solution in 90 per cent. alcohol gave the following numbers:

$c = 10$; $l = 2$ dcm.; $\alpha_D = 3°37'$; $t = 20°$; whence $[\alpha]_D = +18·05°$.

The above number is the mean of two closely agreeing observations, working with different specimens of the acid.

When solutions of the metallic salts indicated below were added to an aqueous solution of sodium santalenate, the following results were observed:

Copper sulphate	A pale blue precipitate.
Nickel sulphate	A pale green precipitate.
Magnesium sulphate	No reaction.
Zinc sulphate	A white precipitate.
Silver nitrate	A white, curdy precipitate.
Mercuric chloride	A white precipitate.
Mercurous nitrate	A white, granular precipitate.
Ferric chloride.....	A buff-coloured, granular precipitate.

Sodium Salt.—This salt was prepared by neutralising a solution of the acid in dilute alcohol with caustic soda, and is soluble both in alcohol and in water.

0·649 gave 0·198 Na_2SO_4. Na = 9·88.

$C_{13}H_{19}O_2Na$ requires Na = 10·00 per cent.

Potassium Salt.—Prepared in a similar manner to the sodium salt. It forms a roughly crystalline, deliquescent mass, soluble in alcohol and in water.

0·332 gave 0·117 K_2SO_4. K = 15·81.

$C_{13}H_{19}O_2K$ requires K = 15·86 per cent.

Ammonium Salt.—The acid dissolves in dilute aqueous ammonia, but on evaporating the solution ammonia is given off and a residue of the acid left.

Silver Salt.—On adding silver nitrate to solutions of any of the foregoing salts, a white, curdy precipitate is formed which is but slightly soluble in water and not greatly affected by light. After being dried in a vacuum over sulphuric acid, it was analysed with the following result:

0·2087 gave 0·0725 Ag. Ag = 34·74.

$C_{13}H_{19}O_2Ag$ requires Ag = 34·29 per cent.

Barium Salt.—This salt may be obtained either by adding barium chloride to a strong solution of the sodium or potassium salt, or by

neutralising a solution of the acid in dilute alcohol with baryta. It is very appreciably soluble in water.

0·098 gave 0·042 $BaSO_4$. Ba = 25·20.
$(C_{13}H_{19}O_2)_2Ba$ requires Ba = 24·86 per cent.

Strontium Salt.—Prepared in a similar manner to the barium salt. It is more soluble in water and more distinctly crystalline than the latter.

0·101 gave 0·037 $SrSO_4$. Sr = 17·46.
$(C_{13}H_{19}O_2)_2Sr$ requires Sr = 17·39 per cent.

The *calcium*, *lead*, and *copper* salts were also prepared and analysed with the following results :

$(C_{13}H_{19}O_2)_2Ca$	requires	Ca = 8·81.	Found Ca = 9·10 per cent.
$(C_{13}H_{19}O_2)_2Pb$	,,	Pb = 33·33.	,, Pb = 33·70 ,,
$(C_{13}H_{19}O_2)_2Cu$	,,	Cu = 13·29.	,, Cu = 13·36 ,,

Methyl Ester, $C_{13}H_{19}O_2{\cdot}CH_3$.—Dry hydrogen chloride was passed into a well-cooled solution of the acid in about six times its weight of methyl alcohol. When the gas ceased to be absorbed, the contents of the retort were poured into water and the excess of hydrochloric acid carefully neutralised with soda. The precipitated methyl santalenate was then extracted with ether, the ethereal solution dried over calcium chloride, and the ether separated by distillation. The methyl ester then remaining was purified by distillation under reduced pressure, almost the whole of it boiling at 232—234° under 35 mm.

It is a colourless, oily liquid, possessing a faint but agreeable smell, and has a sp. gr. 1·0132 at 15°/15°. It is lævorotatory, producing a rotation of −18°13′ in a 100 mm. tube at 20°. On analysis, the following results were obtained :

0·166 gave 0·460 CO_2 and 0·144 H_2O. C = 75·6 ; H = 9·63.
$C_{14}H_{22}O_2$ requires C = 75·67 ; H = 9·91 per cent.

Bromine Derivative.—Santalenic acid was heated with an excess of bromine in chloroform solution for two days under a reflux condenser, hydrogen bromide being liberated in considerable quantity. On distilling off the chloroform, an oily residue was left, which on standing solidified to a crystalline mass. Very great difficulty was experienced in purifying this by crystallisation, owing to its great solubility in almost all the ordinary organic solvents, and to its marked tendency to separate as an oil. From a mixture of benzene and light petroleum, however, small needle-shaped crystals were obtained, but they were undoubtedly still contaminated with some of the bye-products of the bromination process, and attempts to further purify them failed. These

crystals melted at 114—115°, and contained Br = 40·8 per cent., a dibromosantalenic acid of the formula $C_{13}H_{18}O_2Br_2$ requiring Br = 43·71 per cent.

In the oxidation experiments above described, the filtrates from the santalenic acid on extraction by ether yielded an oily acid liquid having a peculiar and characteristic odour. The silver salt prepared from this, darkened rapidly on exposure to light, and was much more soluble in water than silver santalenate. This acid is now being studied. Acetic acid and carbon dioxide were also produced in small quantities.

It seems not improbable that a further study of the derivatives and decomposition products of santalenic acid may throw some light upon the constitution of the so-called santalols which form the chief constituents of the oil.

XIV.—*The Interaction of Ethyl Sodiomethylmalonate and Mesityl Oxide.*

By Arthur William Crossley.

Experiments undertaken with the object of synthesising dihydrocamphoric acid (Trans., 1898, **73**, 5, 23) have already been described by the author (Trans., 1899, **75**, 771). Although non-success has attended further efforts to prepare this acid, several new and interesting substances have been encountered, and are described in the present communication (compare Proc., 1900, **16**, 90), of which the main object was the preparation of a ketonic acid of the formula

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(CH_3)_2{\cdot}CH(CH_3){\cdot}CO_2H.$$

It was then intended to add on the elements of hydrogen cyanide to the ketonic group, ultimately obtaining a substituted adipic acid.

Vorländer (*Annalen*, 1897, **294**, 317) has shown that several of the substituted dihydroresorcinols undergo hydrolysis, with rupture of the ring, when treated with either barium hydroxide or dilute mineral acids. For example, phenyldihydroresorcinol gives rise to β-phenyl-γ-acetobutyric acid when treated in this manner:

$$C_6H_5{\cdot}CH\begin{<}{CH_2{\cdot}CO\atop CH_2{\cdot}CO}\end{>}CH_2 + H_2O = C_6H_5{\cdot}CH\begin{<}{CH_2{\cdot}CO_2H\atop CH_2{\cdot}CO{\cdot}CH_3}.$$

It seemed possible, therefore, that the ketonic acid just mentioned might be obtained by hydrolysis of trimethyldihydroresorcinol (2 : 6-diketo-3 : 4 : 4-trimethylhexamethylene):

$$(CH_3)_2C\begin{<}{CH(CH_3){\cdot}CO\atop CH_2\text{——}CO}\end{>}CH_2 + H_2O = (CH_3)_2C\begin{<}{CH(CH_3){\cdot}CO_2H\atop CH_2{\cdot}CO{\cdot}CH_3}.$$

This substance may be readily prepared in large quantities by hydrolysing the compound formed by the condensation of ethyl sodiomethylmalonate and mesityl oxide :

$$(CH_3)_2C{:}CH{\cdot}CO{\cdot}CH_3 + NaC(CH_3)(CO_2Et)_2 =$$
$$(CH_3)_2C\!<\!\begin{matrix}C(CH_3)(CO_2Et){\cdot}CO\\ CH_2\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!CO\end{matrix}\!>\!CH_2 + EtOH.$$

$$(CH_3)_2C\!<\!\begin{matrix}C(CH_3)(CO_2Et){\cdot}CO\\ CH_2\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!CO\end{matrix}\!>\!CH_2 + H_2O =$$
$$(CH_3)_2C\!<\!\begin{matrix}CH(CH_3){\cdot}CO\\ CH_2\!-\!\!-\!\!-\!CO\end{matrix}\!>\!CH_2 + CO_2 + EtOH.$$

I.

That this substance, I, has the constitution ascribed to it, is proved, not only by its method of formation, but also by the facts that it gives the characteristic reactions of substituted resorcinols, and is converted on oxidation with sodium hypobromite into *αββ*-trimethylglutaric acid :

$$(CH_3)_2C\!<\!\begin{matrix}CH(CH_3){\cdot}CO\\ CH_2\!-\!\!-\!\!-\!CO\end{matrix}\!>\!CH_2 \longrightarrow (CH_3)_2C\!<\!\begin{matrix}CH(CH_3){\cdot}CO_2H\\ CH_2{\cdot}CO_2H\end{matrix}.$$

Up to the present, however, it has not been possible to hydrolyse this substance and produce the desired ketonic acid by splitting the ring. It may, for example, be recovered quantitatively after boiling for 16 hours with excess of barium hydroxide. On boiling with dilute sulphuric acid, it appears to suffer some change, and the question of its hydrolysis is still being investigated.

Like the dihydroresorcinols already described (Merling, *Annalen*, 1894, **278**, 20 ; Vorländer, *ibid.*, 1897, **294**, 302), 2 : 6-*diketo*-3 : 4 : 4-*trimethylhexamethylene* behaves in some respects as a diketone, giving, for example, a well-defined dioxime :

$$(CH_3)_2C\!<\!\begin{matrix}CH(CH_3){\cdot}C(NOH)\\ CH_2\!-\!\!-\!\!-\!C(NOH)\end{matrix}\!>\!CH_2.$$

It may also react as Δ^6-6-*hydroxy*-2-*keto*-3 : 4 : 4-*trimethylhexamethylene* (and this appears to be its most usual form) :

$$(CH_3)_2C\!<\!\begin{matrix}CH(CH_3){\cdot}CO\\ CH_2\!-\!C(OH)\end{matrix}\!>\!CH,$$

when, for example, it yields a silver salt, and this on treatment with ethyl iodide gives an ethyl ether :

$$(CH_3)_2C\!<\!\begin{matrix}CH(CH_3){\cdot}CO\\ CH_2\!-\!C(OAg)\end{matrix}\!>\!CH + C_2H_5I =$$
$$AgI + (CH_3)_2C\!<\!\begin{matrix}CH(CH_3)\!-\!\!-\!CO\\ CH_2{\cdot}C(OC_2H_5)\end{matrix}\!>\!CH.$$

Towards phosphorus pentachloride, however, it behaves as $\Delta^{2,6}$-2 : 6-

dihydroxy-3 : 4 : 4-*trimethyldihydroresorcinol* (formula I), giving rise to $\Delta^{2,6}$-2 : 6-*dichloro*-3 : 4 : 4-*trimethyldihydrobenzene* (formula II), where both oxygen atoms have been removed as hydroxyl groups.

I. $(CH_3)_2C<\begin{matrix}C(CH_3):C(OH)\\CH_2\text{——}C(OH)\end{matrix}>CH$. II. $(CH_3)_2C<\begin{matrix}C(CH_3):CCl\\CH_2\text{——}CCl\end{matrix}>CH$.

This behaviour is peculiar, as apparently no derivatives of dihydroresorcinol or substituted dihydroresorcinols have been described in which these compounds react as though they contained two hydroxyl groups.

Dihydroresorcinol gives a monoacetyl derivative,

$$CH_2<\begin{matrix}CH_2\text{——}CO\\CH_2\cdot C(OAc)\end{matrix}>CH,$$

but Merling states (*loc. cit.*, 23) that he was unable to obtain a diacetyl derivative. On this account, the action of the phosphorus haloids and other reagents towards substituted dihydroresorcinols is being thoroughly investigated.

The unsaturated nature of diketotrimethylhexamethylene (hydroxyketonic form) is shown by its behaviour towards bromine, when it takes up two atomic proportions forming *dibromohydroxyketotrimethylhexamethylene* (formula III.). This is a highly unstable compound, readily losing hydrogen bromide to form 1-*bromo*-2 : 6-*diketo*-3 : 4 : 4-*trimethylhexamethylene* (formula IV), from which, conversely, it may be prepared by the direct addition of the elements of hydrogen bromide.

$$(CH_3)_2C<\begin{matrix}CH(CH_3)\text{—}CO\\CH_2\cdot CBr(OH)\end{matrix}>CHBr,$$

III.

$$(CH_3)_2C<\begin{matrix}CH(CH_3)\cdot CO\\CH_2\text{—}C(OH)\end{matrix}>CBr, \text{ or } (CH_3)_2C<\begin{matrix}CH(CH_3)\cdot CO\\CH_2\text{——}CO\end{matrix}>CHBr.$$

IV.

When treated with an insufficient amount of sodium hypobromite for complete oxidation, diketotrimethylhexamethylene is converted into a dibromo-derivative to which the following constitution is assigned :

$$(CH_3)_2C<\begin{matrix}CH(CH_3)\cdot CO\\CH_2\text{——}CO\end{matrix}>CBr_2,$$

because when treated with potash alone it is converted into $\alpha\beta\beta$-trimethylglutaric acid and monobromodiketotrimethylhexamethylene (formula IV), and when oxidised with sodium hypobromite is quantitatively changed into $\alpha\beta\beta$-trimethylglutaric acid and bromoform.

Experimental.

Ethyl 2 : 6-*Diketo*-3 : 4 : 4-*trimethylhexamethylene*-3-*carboxylate*,

$$(CH_3)_2C\begin{cases}C(CH_3)(CO_2C_2H_5)\cdot CO\\ CH_2\end{cases}\!\!>\!\!\!

Ethyl diketotrimethylhexamethylenecarboxylate dissolves only slightly in hot water or light petroleum, but is readily soluble in other ordinary organic solvents. When slowly crystallised from a mixture of chloroform and light petroleum, it comes down in large, six-sided prisms, but is most readily obtained pure as described above. The yield (53 per cent. of the theoretical) cannot well be compared with that of the ester obtained by condensing ethyl malonate and mesityl oxide, for it is impossible to say how much unchanged ethyl malonate was contained in the ethyl methylmalonate employed.

The ester may be distilled under diminished pressure with but very slight decomposition, and boils at 190° under 31 mm. Its aqueous solution is coloured violet-red by addition of ferric chloride.

When treated in alcoholic solution with an acetic acid solution of semicarbazide, it yields a *semicarbazone* separating from dilute ethyl alcohol in crystalline nodules, melting at 206° with decomposition and evolution of gas.

0·1594 gave 20·4 c.c. moist nitrogen at 14° and 760 mm. N = 15·06.
$C_{13}H_{21}O_4N_3$ requires N = 14·84 per cent.

C. This thick, dark-coloured oil showed no signs of solidifying after standing in a vacuum for many weeks, so it was hydrolysed with alcoholic potash, acidified with sulphuric acid, extracted with ether, and the residue left after evaporation of the ether distilled in a vacuum. Two main fractions were obtained, boiling respectively at 140—150° and 170—175° under 41 mm. pressure, and a considerable residue remained which, on cooling, set to a red resin (compare Trans., 1899, 75, 773).

The fraction boiling at 140—150° under 41 mm. pressure smelt strongly of fatty acids, and on distilling in air separated into two portions, boiling about 118° and 140° respectively and although not further investigated, evidently consisted of acetic and propionic acids, produced by the hydrolysis of unaltered ethyl malonate and ethyl methylmalonate.

The fraction boiling at 170—175° under 41 mm. pressure solidified completely, and by repeated crystallisation from a mixture of chloroform and light petroleum two compounds were isolated melting at 148° (with production of a red film) and 100°. These are the melting points respectively of 2 : 6-diketo-4 : 4-dimethylhexamethylene (dimethyldihydroresorcinol) and 2 : 6-diketo-3 : 4 : 4-trimethylhexamethylene (see page 143), the occurrence of the former being due to the presence of ethyl malonate in the ethyl methylmalonate employed in the condensation experiment.

2 : 6-*Diketo*-3 : 4 : 4-*trimethylhexamethylene* (2 : 6-*Dihydroxy*-3 : 4 : 4-*trimethyldihydroresorcinol*), $(CH_3)_2C<\begin{matrix}CH(CH_3)\cdot CO\\CH_2\text{——}CO\end{matrix}>CH_2$.

One hundred and fifteen grams of ethyl 2 : 6-diketo-3 : 4 : 4-trimethylhexamethylene-3-carboxylate were hydrolysed by heating for 12 hours with 170 grams of pure potassium hydroxide dissolved in alcohol. Water was then added, the alcohol evaporated, and the whole acidified with dilute sulphuric acid. A small amount of material separated, which was insoluble in water or ether, but on boiling with water, carbon dioxide was evolved, and diketotrimethylhexamethylene remained, so the substance probably consisted of *diketotrimethylhexamethylenecarboxylic acid*. The acidified solution was then extracted with ether, &c., when 75 grams (calculated 78) of a solid were obtained, which was purified by crystallisation from a mixture of chloroform and light petroleum (b. p. 40—60°) and analysed :

0·1172 gave 0·3012 CO_2 and 0·0970 H_2O. C = 70·08 ; H = 9·19.
$C_9H_{14}O_2$ requires C = 70·13 ; H = 9·09 per cent.

Diketotrimethylhexamethylene is sparingly soluble in water or light petroleum, but dissolves readily in the ordinary organic solvents. It crystallises from the above mixture in radiating clusters of needles melting at 99·5—100°. When heated in a capillary tube above its melting point, it does not give rise to a red film like the dimethyl derivative, but at 200—210° evolves gas, becomes light brown in colour, and does not resolidify on cooling. Its aqueous solution has an intensely acid reaction, effervesces with sodium hydrogen carbonate, and gives a violet-red coloration with ferric chloride.

The *silver salt*, $C_9H_{13}O_2Ag$, prepared in the usual manner, is a white, flocculent precipitate almost insoluble in water.

0·2402 gave, on ignition, 0·0990 Ag. Ag = 41·21.
$C_9H_{13}O_2Ag$ requires Ag = 41·38 per cent.

The *dioxime*, $C_9H_{16}O_2N_2$, was obtained by adding the calculated quantities of hydroxylamine hydrochloride and sodium hydroxide, dissolved in the smallest possible quantity of water, to an alcoholic solution of the ketone. On standing, the solution became violet and gradually deposited crystals, which were filtered off, treated with animal charcoal, and recrystallised from dilute ethyl alcohol, from which solvent they separate in colourless, four-sided pyramids melting at 167°. It is insoluble in chloroform or benzene, but readily soluble in methyl or ethyl alcohol on warming.

0·1994 gave 27 c.c. moist nitrogen at 17° and 760 mm. N = 15·71.
$C_9H_{16}O_2N_2$ requires N = 15·22 per cent.

The *ethyl ether*, $(CH_3)_2C<\begin{matrix}CH(CH_3)—CO\\CH_2\cdot C(OC_2H_5)\end{matrix}>CH$, was prepared by heating the dry silver salt suspended in dry ether with the calculated amount of ethyl iodide in a reflux apparatus for 3 hours. The oil obtained by evaporating the filtered ethereal solution did not solidify even after long standing. It was therefore purified by distillation and analysed:

0·1182 gave 0·3127 CO_2 and 0·1036 H_2O. C = 72·16; H = 9·74.
$C_{11}H_{18}O_2$ requires C = 72·52; H = 9·90 per cent.

The ether is a faintly yellow, thick, oily liquid boiling at 265° under 750 mm. pressure. It is insoluble in cold sodium carbonate solution, and when hydrolysed with alcoholic potassium hydroxide is quantitatively reconverted into diketotrimethylhexamethylene.

Action of Phosphorus Pentachloride on $\Delta^{2,6}$-2 : 6-*Dihydroxy*-3 : 4 : 4-*trimethyldihydroresorcinol.*

Five grams of the resorcinol were mixed with 14 grams of phosphorus pentachloride. A moderate action at once set in with formation of a yellow solution, which was heated on a water-bath for half an hour to complete the reaction, during which time remarkable colour changes took place. The yellow solution first changed to olive-green, and then successively to brown, green, indigo-blue, nearly black, and finally reddish-brown. The whole was then slowly poured into water and extracted with ether, the ethereal solution washed with water, dried over calcium chloride, and the ether evaporated, when a thick brown liquid was obtained which rapidly deposited crystals. These were drained off,* purified by crystallisation from methyl alcohol, and analysed:

0·1400 gave 0·2914 CO_2 and 0·0740 H_2O. C = 56·77; H = 5·90.
0·1504 „ 0·2260 AgCl. Cl = 37·17.
$C_9H_{12}Cl_2$ requires C = 56·54; H = 6·28; Cl = 37·17 per cent.

$\Delta^{2,6}$-2 : 6-*Dichloro*-3 : 4 : 4-*trimethyldihydrobenzene*,

$$(CH_3)_2C<\begin{matrix}C(CH_3):CCl\\CH_2—CCl\end{matrix}>CH,$$

thus obtained, is insoluble in water, but very soluble in the cold in benzene, light petroleum, or acetone, and in methyl or ethyl alcohol on warming. From the last-named solvent it crystallises in beautiful, long, flattened, glistening needles melting at 77°.

* The filtrate from these crystals boils undecomposed at 120—125° under 31 mm. pressure, but its properties have not yet been further examined.

Action of Bromine on Diketotrimethylhexamethylene.

To a solution of diketotrimethylhexamethylene in dry chloroform, a solution of bromine in dry chloroform was added in the dark, until the colour of the bromine was no longer destroyed, when hydrogen bromide was freely evolved. The whole was placed in a vacuum over potassium hydroxide, when it slowly solidified. After purification by spreading on porous plates and crystallisation from benzene, the substance was analysed :

0·2366 gave 0·1899 AgBr. Br = 34·15.

$C_9H_{13}O_2Br$ requires Br = 34·33 per cent.

1-*Bromo*-2 : 6-*diketo*-3 : 4 : 4-*trimethylhexamethylene*,

$$(CH_3)_2C\begin{<}CH(CH_3)\cdot CO\\CH_2\text{——}CO\end{>}CHBr,$$

is insoluble in light petroleum, moderately soluble in hot water or benzene, and very soluble in alcohol, acetone, or ethyl acetate. It crystallises from benzene in stellar aggregates of colourless, transparent, glistening plates melting at 151·5° with decomposition and evolution of gas. When dissolved in dilute aqueous potassium hydroxide and treated with sodium amalgam, it is quantitatively reconverted into diketotrimethylhexamethylene melting at 100°, and when oxidised with sodium hypobromite it is converted into $\alpha\beta\beta$-trimethylglutaric acid (see p. 147).

If during the addition of bromine the whole is cooled in ice, comparatively little hydrogen bromide is evolved, and after standing for some time a white, crystalline powder is deposited, which on exposure to air rapidly evolves hydrogen bromide. It was therefore filtered off by the aid of a pump, washed with light petroleum, dried as rapidly as possible, and the bromine determined :

0·1986 gave 0·2450 AgBr. Br = 52·41.

$C_9H_{14}O_2Br_2$ requires Br = 50·95 per cent.

Additional bromine determinations in separate preparations gave :

Br = 53·34, 52·21, and 52·95 per cent.

The amount of hydrogen bromide evolved on keeping the substance in a vacuum over potassium hydroxide was also determined, but was always in excess of that calculated :

1·8530 lost 0·5266 HBr. HBr = 28·42.

1·8304 „ 0·5225 HBr. HBr = 28·54.

Calculated loss of HBr = 25·80 per cent.

Although the numbers obtained do not agree either with the calcu-

lated amount or with one another, they are sufficiently close to point to the fact that this substance is a dibromide formed by the direct addition of two atomic proportions of bromine to the hexamethylene derivative.

1 : 6-*Dibromo*-6-*hydroxy*-2-*keto*-3 : 4 : 4-*trimethylhexamethylene*,

$$(CH_3)_2C<\begin{matrix}CH(CH_3)-CO\\CH_2\cdot CBr(OH)\end{matrix}>CHBr,$$

is a white, crystalline powder melting sharply at 87—88°. It cannot be obtained pure because it only separates from a solution containing excess of hydrogen bromide, and on attempting to crystallise it from any solvent, hydrogen bromide is evolved, and the above described monobromo-derivative melting at 151·5° separates out. It seemed probable, therefore, that this dibromide would be formed by the direct addition of hydrogen bromide to monobromodiketotrimethylhexamethylene, which proved to be the case, for if the latter is dissolved in dry chloroform and the solution after cooling in ice is saturated with hydrogen bromide, on standing a crystalline powder separates melting at 87—88° and having identical properties with the above dibromo-derivative.

Action of Sodium Hypobromite on 2 : 6-*Diketo*-3 : 4 : 4-*trimethylhexamethylene.*

Fifty grams of bromine were poured into 300 c.c. of water cooled to 0°, and a strong solution of sodium hydroxide was then slowly added until the colour of the bromine had disappeared. A solution of 12 grams of diketotrimethylhexamethylene in sodium hydroxide (14 grams NaOH in 80 c.c. of water) was then poured in and the whole allowed to stand for 2½ hours. The solution, after separation from carbon tetrabromide and bromoform, was acidified with hydrochloric acid, when a copious white precipitate (10 grams) was formed which was collected (filtrate = A), purified by crystallisation from alcohol, and analysed :

0·1560 gave 0·1883 AgBr. Br = 51·34.
0·1554 „ 0·1868 AgBr. Br = 51·15.
$C_9H_{12}O_2Br_2$ requires Br = 51·28 per cent.

1 : 1-*Dibromo*-2 : 6-*diketo*-3 : 4 : 4-*trimethylhexamethylene*,

$$(CH_3)_2C<\begin{matrix}CH(CH_3)\cdot CO\\CH_2\text{——}CO\end{matrix}>CBr_2,$$

is readily soluble in cold chloroform, acetone, or ethyl acetate, but less so in hot alcohol, light petroleum, or water. It crystallises from alcohol in well-formed white needles melting at 112·5° without any sign of decomposition, and resolidifies at 110°. When boiled with aqueous potassium hydroxide, it dissolves and bromoform separates.

On acidifying the filtered solution with hydrochloric acid, a white solid separates which was collected (filtrate = B) and purified by crystallisation from benzene, when it was found to melt at 151·5° with decomposition and evolution of gas, and had properties identical with monobromodiketotrimethylhexamethylene (see page 145).

A portion of the dibromo-derivative (m. p. 151·5°) was then further treated with sodium hypobromite. The resulting liquid, separated from bromoform, gave no precipitate on acidification with hydrochloric acid, but after evaporation and extraction with ether, &c., *αββ*-trimethylglutaric acid melting at 87° was obtained.

The filtrates A and B, on evaporation and extraction with ether, gave further quantities of the same glutaric acid.

If when treating the hexamethylene derivative with sodium hypobromite the above quantities are slightly varied (the proportions which give the best results are: 80 grams of bromine in 1000 c.c. of water, decolorised with sodium hydroxide; and 20 grams of diketotrimethylhexamethylene in a solution of 30 grams of sodium hydroxide in 150 c.c. of water), then on acidifying with hydrochloric acid no solid separates. On evaporation and extraction with ether, &c., a solid substance is obtained which dissolves completely in water with a very acid reaction, and on saturating the solution with hydrogen chloride, crystallises out in beautiful leaflets melting at 87—88°.

0·1109 gave 0·2231 CO_2 and 0·0802 H_2O. C = 54·86; H = 8·03.
$C_8H_{14}O_4$ requires C = 55·17; H = 8·04 per cent.

In order to further compare this substance with the *αββ-trimethylglutaric acid* described by Perkin and Thorpe (Trans., 1899, 75, 65), it was converted into the anhydride and this into the *anilic acid*, which crystallised from dilute methyl alcohol in stout needle-shaped crystals melting at 150°.

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XV.—*Ammonium Bromide and the Atomic Weight of Nitrogen.*

By Alexander Scott.

Although the whole of the recent work on the ratio of the atomic weights of hydrogen and oxygen relatively to one another seems to establish that ratio as 1 : 15·88 or 1·0075 : 16, I thought it would be not only of great interest, but of the highest importance if this ratio

could be determined in some manner totally different from any that had been previously attempted and depending in no way on determinations of the composition of water.

The ideal method was to find some atom or group of atoms which unites with hydrogen and with oxygen to produce compounds of sufficient stability for their equivalent weights to be accurately determined. We seem to have this in the three bases—hydrazine, ammonia, and hydroxylamine, which for this purpose may be regarded as having the formulæ NH_2, NH_3, NH_3O, hydrazine having one hydrogen atom less and hydroxylamine one oxygen atom more than ammonia.

The hydrobromides of these bases seem from their general properties admirably adapted for comparison with one another by determining in each case the equivalent amount of pure silver.

Although the preparation and purification of the substances and the necessary careful study of their adaptability for the end in view has occupied rather more than two years, it was not anticipated that any serious difficulty would occur in the case of the central member of the group, ammonium bromide. Nevertheless, such is the case, and the explanation of the discrepancies which exist between the classical work of Stas and my own is by no means easy.

Stas (*Œuvres*, 1, 812) gives the ratio of ammonium bromide to silver as 98·032:107·93, whereas I find only 97·995 : 107·93 ; the corresponding values for ammonium are 18·077 and 18·040, and for the atomic weight of nitrogen 14·047 and 14·010.

Stas deduced the value above stated from seven experiments on samples of ammonium bromide prepared in different ways and apparently always against the same sample of silver.

He states (*loc. cit.*, p. 790) "On le sait, le bromure d'ammonium peut être volatilisé sans décomposition dans un courant de gaz ammoniac sec. Dans le but de me procurer ce sel à l'état compacte et partant facile à peser et à manier, j'ai essayé d'avoir recours à cette volatilisation, mais après plusieurs tentatives infructueuses, j'ai été obligé d'y renoncer. En effet, à une température très-peu supérieure à sa volatilisation, il se dissocie, du brome même devient parfois libre. On constate aisément la présence de ce corps par la coloration de la vapeur du bromure, et *par la coloration en jaune du sel condensé*, qui a produit des fumées lorsqu'on l'a chauffé dans de l'ammoniaque seche."

The italics are those of Stas himself. He further remarks that his bromide, which was brilliantly white and remained so indefinitely at the ordinary temperature under a bell jar over potash, lost its whiteness and became greyish (*grisâtre*) when heated in air at temperatures above 100°, that this greyness increased as the salt was heated from 115° to 180°, and that the whiteness was only partially restored by heating it in a current of ammonia.

All my samples were also brilliantly white and showed no greyness when heated in air to 180°, although they lost their sparkling whiteness; this was due, however, to a change in the surface of the crystals owing to the slight sublimation which takes place when the salt, imperfectly dried, is heated to that temperature. No difficulty was experienced in subliming the salt either in a vacuum, in a mixture of ammonia and hydrogen, or in pure ammonia itself, and no trace of yellow coloration was observed in any instance, the condensed salt being a somewhat horny, translucent mass.

The silver employed was prepared from the pure silver of commerce by dissolving it in nitric acid, evaporating the solution to dryness, and fusing the salt for twenty minutes, the fused mass was then dissolved in water, filtered and kept gently boiling for several hours with 10 to 15 grams of freshly precipitated silver oxide, the oxides of lead, copper, and iron being thus precipitated and apparently completely removed.

After filtration, the solution of silver nitrate thus purified was added in small quantities at a time to a solution of equivalent quantities of ammonium formate and acetate sufficient to reduce rather more than the total silver nitrate added. The solution of ammonium formate and acetate was made by distilling pure formic and pure acetic acids into a solution of ammonia (which had been prepared by passing well washed ammonia into pure redistilled water in a porcelain beaker) until the solution was strongly acid; everything of a nature not very easily volatile was thus completely excluded from the reducing agent. It was suitably diluted and raised to the boiling point in a flask of special non-attackable glass and the silver nitrate solution added. The reaction which takes place is:

$$HCO_2NH_4 + 2AgNO_3 = NH_4NO_3 + HNO_3 + 2Ag + CO_2$$

and $$CH_3{\cdot}CO_2NH_4 + HNO_3 = NH_4NO_3 + CH_3{\cdot}CO_2H,$$

the use of the ammonium acetate being merely to exchange the liberated nitric for acetic acid. After being thoroughly washed and dried, the silver was fused with a little pure sodium and potassium carbonates along with a little nitre, granulated, and the above process repeated, the reprecipitated and thoroughly washed silver being raised to a low red heat in a muffle and kept in the easily divided form thus obtained. Only two or three milligrams of ferric oxide were separated by the second treatment from a kilogram of silver.

This silver was notably better than a sample prepared with the utmost care by the cuprous ammonium sulphite method so much employed for the purification of silver.

The hydrobromic acid employed was made in two ways: (1) by distilling potassium bromide with somewhat diluted sulphuric acid and frequent redistillation (Squibb's process), and (2) by the reduction of

bromine to hydrobromic acid by means of sulphurous acid, as I have described (Trans., 1900, 77, 649).

The ammonia was also from two sources: (1) from ammonium sulphate drastically treated with nitric and sulphuric acids, and (2) from potassium nitrite reduced by means of zinc which had been fused with lead oxide. In both cases, all the precautions given by Stas were rigorously adhered to and in some cases even exceeded.

The balance chiefly employed in the weighings was an excellent one by Bunge and the weights were of platinium-iridium made by Messrs. Johnson, Matthey & Co. and adjusted with great accuracy by Oertling.

The silver, after being heated over a spirit burner in pure hydrogen and weighed, was dissolved in a carefully stoppered bottle in pure nitric acid (sp. gr. 1·42), the bottle standing on the water-bath for an hour. After complete cooling, the pressure inside the bottle was almost always considerably less than that of the atmosphere, so that water could be drawn in when the stopper was carefully removed and all possible loss of silver thus avoided.

The silver nitrate solution was then diluted and kept on the water-bath until both the solution and the atmosphere above it were quite colourless.

The ammonium bromide, heated in almost every case to 180° for some hours in a current of hydrogen which had been bubbled through pure ammonia solution and dried by passing over solid soda and metallic sodium, was weighed after being cooled in a vacuum, then dissolved and added to the silver solution in a room lit with red light only, the whole vigorously shaken, and this shaking frequently repeated. The excess of silver or bromide remaining in solution was determined (usually after two days) by means of standard solutions (which were in all cases weighed).

In the following summary all the weights given are reduced to vacuum weighings, and corrected for all errors in the face values of the weights. The atomic weight of silver is taken as 107·93.

To test the effect of sublimation on the salt, the third crop of crystals obtained by evaporating to dryness the mother liquors from the ammonium bromide used in series IV and V below was employed. Obtained in this way, it was likely to be abnormally acid, and therefore would tend to give a low equivalent.

(a). Not sublimed, dried in hydrogen and ammonia at 180°.

$$4{\cdot}89631\ NH_4Br = 5{\cdot}39380\ Ag \quad \therefore\ NH_4Br = \mathbf{97{\cdot}975}.$$

(b). Sublimed once in Sprengel vacuum, but not dried or treated further.

$$2{\cdot}45925\ NH_4Br = 2{\cdot}70914\ Ag \quad \therefore\ NH_4Br = \mathbf{97{\cdot}972}.$$

(c). Sublimed twice in Sprengel vacuum, and dried in hydrogen and ammonia at 180°.

$$3{\cdot}29478\ NH_4Br = 3{\cdot}62928\ Ag \therefore NH_4Br = 97{\cdot}982.$$

(d). Sublimed in hydrogen and ammonia and heated in the same at 180° for some hours.

$$4{\cdot}46957\ NH_4Br = 4{\cdot}92273\ Ag \therefore NH_4Br = 97{\cdot}994.$$

(a), (b), and (c) show by their low equivalents that they were distinctly acid, which acidity was only overcome by sublimation in a strongly ammoniacal atmosphere.

The other samples of ammonium bromide were crystallised from *alkaline* solutions. The solutions of the dried bromide, like those of Stas, were all strongly acid to litmus.

I. Ammonia from ammonium sulphate. Hydrobromic acid from potassium bromide. Silver reduced by formate.

(a). $4{\cdot}20661\ NH_4Br = 4{\cdot}63303\ Ag \therefore NH_4Br = 97{\cdot}996.$
(b). $4{\cdot}23664\ NH_4Br = 4{\cdot}66644\ Ag \therefore NH_4Br = 97{\cdot}989.$

II. Ammonia from potassium nitrite. Hydrobromic acid from potassium bromide. Silver reduced by formate.

(a). $4{\cdot}31464\ NH_4Br = 4{\cdot}75175\ Ag \therefore NH_4Br = 98{\cdot}001.$
(b). $6{\cdot}19233\ NH_4Br = 6{\cdot}82047\ Ag \therefore NH_4Br = 97{\cdot}990.$

III. Same ammonium bromide as in I. Silver reduced by cuprous ammonium sulphite.

$$8{\cdot}77664\ NH_4Br = 9{\cdot}66788\ Ag \therefore NH_4Br = 97{\cdot}981.$$

This silver was found to contain 0·0018 gram of ferric oxide, hence the true equivalent weights are:

$$8{\cdot}77664\ NH_4Br = 9{\cdot}66608\ Ag \therefore NH_4Br = 97{\cdot}999.$$

IV. Ammonia from ammonium sulphate. Hydrobromic acid from pure bromine. *First* crop of crystals. Silver reduced by formate *unfused*.

(a). $10{\cdot}47233\ NH_4Br = 11{\cdot}53416\ Ag \therefore NH_4Br = 97{\cdot}994.$

Same, but the silver *fused* on pure calcium phosphate cupel.

(b). $4{\cdot}91997\ NH_4Br = 5{\cdot}41834\ Ag \therefore NH_4Br = 98{\cdot}0028.$

V. Ammonia from ammonium sulphate. Hydrobromic acid from pure bromine. *Second* crop of crystals. Silver reduced by formate.

The ammonium bromide was sublimed in a current of pure ammonia, and allowed to cool for 4 hours in it at the atmospheric pressure, then left in a vacuum for 36 hours over sulphuric acid. It was then divided

into two portions, one of which was left 54 hours longer over sulphuric acid in a vacuum, when

(a). 5·00442 NH_4Br = 5·51164 Ag ∴ NH_4Br = **97·997.**

The other portion was dried as usual in hydrogen and ammonia at 180°, when

(b). 5·17914 NH_4Br = 5·70390 Ag ∴ NH_4Br = **98·000.**

VI. In order to test in the severest manner possible the quality of the silver employed, at the suggestion of Professor Dewar I reduced the silver bromide obtained in series IV (a) by pure hydrogen; one part of this was fused on a pure calcium phosphate cupel by means of a mouth blow-pipe of glass fed by pure hydrogen, and cooled in hydrogen, then thoroughly cleaned by treatment first with pure hydrochloric acid and then with ammonia, and heated for some time in hydrogen. When compared with the ammonium bromide of series IV, it was found:

(a). 4·84099 NH_4Br = 5·33177 Ag ∴ NH_4Br = **97·995.**

The other portion was fused on a cupel of pure lime made as Richards recommends by igniting a mixture of 3 parts of pure lime and 1 part of pure calcium nitrate, and treated as above. It was weighed and then heated for nearly an hour in a Sprengel vacuum at the boiling point of sulphur, and afterwards to as high a temperature as the combustion tube would stand, and cooled in the vacuum. Its weight was unchanged, and no gas was extracted from it.

(b). 5·10677 NH_4Br = 5·62515 Ag ∴ NH_4Br = **97·984.**

This seems to corroborate the statement of Stas that the silver fused on calcium phosphate is purer than that fused on pure calcium oxide. It also looked more brilliant, although the dulness of that fused on the lime was due partly to a small quantity of lime dust floating on the surface.

The silver bromide precipitated was collected after several of the titrations, in order to determine whether the silver and the bromine were strictly comparable with those of Stas. To ensure the whole of the silver being precipitated, a few drops of pure hydrobromic acid were always added. The silver bromide was collected in a porcelain Gooch crucible on a filter of the finest asbestos, which had been very carefully purified by means of sulphuric and nitric acids. It was then heated to 180°, and after an hour or so at this temperature was dried perfectly, even with the largest quantities collected. Fusion of the bromide resulted in the loss of a few tenths of a milligram only, which by blank experiments was shown to be due to the asbestos

filter. No difficulty was encountered in getting both the crucible and filter, and these together with the silver bromide and chloride, to give weights constant to one-tenth of a milligram.

The whole of the filtrate was evaporated to dryness in each case to see if any foreign matter could be detected, or if any silver bromide had passed through. In only one case was anything weighable found, and that was in the case of the silver reduced by means of cuprous ammonium sulphite (series III) when 0·0018 gram of ferric oxide was obtained. The weights of silver bromide are obviously more likely to be too low than too high from experimental errors.

II. (b) 6·82315 Ag gave 11·87733 AgBr.
$\therefore$ 100 Ag = 174·074 AgBr.
Stas found 174·080.

III. 9·66809 Ag gave 16·82816 AgBr.
$\therefore$ 100 Ag = 174·059 AgBr.
corr. for Fe_2O_3 174·090.

IV. (b) 5·41906 Ag gave 9·43315 AgBr.
$\therefore$ 100 Ag = 174·0735 AgBr.

V. (a) 5·51258 Ag gave 9·59596 AgBr.
$\therefore$ 100 Ag = 174·074 AgBr.

(b) 5·70686 Ag gave 9·93346 AgBr.
$\therefore$ 100 Ag = 174·062 AgBr.

VI. (a) 5·33191 Ag gave 9·28093 AgBr.
$\therefore$ 100 Ag = 174·064 AgBr.

(b) 5·62572 Ag gave 9·79254 AgBr.
$\therefore$ 100 Ag = 174·067 AgBr.

A further interesting corroboration of the value found above for ammonium bromide as it involves different samples of ammonia, hydrobromic acid, and silver, as well as personal equation, is that in August, 1882, Mr. C. T. Heycock and the author prepared ammonium bromide which was titrated as above against silver prepared by the cuprous ammonium sulphite method, the titration being done by Mr. Heycock. The mean of two experiments in each of which over 7 grams were used was **97·993**.

As Mr. Heycock was working at the time on the atomic weight of rubidium, and along with Professor Dewar I was working at the atomic weight of manganese, our object in then preparing ammonium bromide was to have a salt which we thought could be prepared easily at any time and used as a standard substance to determine the purity of any sample either of hydrobromic acid or of silver, but as our

value differed from that of Stas, only these two determinations were made, and the salt condemned as unsuitable for our purpose.

Two determinations were made with ammonium chloride; the ammonia was from the purified ammonium sulphate used in the experiments on the bromide, and the hydrochloric acid was the pure acid of commerce diluted till just under constant boiling point strength and boiled gently for some hours, a few crystals of potassium chlorate being added at intervals, all chlorine and chlorine oxides were then expelled by boiling, and the acid distilled first through a glass and then through a platinum condenser.

(a). 4·78257 NH_4Cl = 9·64484 Ag ∴ NH_4Cl = **53·519**.
(b). 5·51744 NH_4Cl = 11·12810 Ag ∴ NH_4Cl = **53·513**.

The silver chloride was collected from (a) when with the standard ammonium chloride solution added, it was found that

4·7850 NH_4Cl gave 12·82048 AgCl.
If AgCl = 143·387 then NH_4Cl = **53·5165**,

which is the mean of the two titration values. The value given by Stas is 53·532.

The situation may be thus summed up:

The values obtained by Stas for the equivalents of ammonium bromide and chloride are **98·032** and **53·532**, whereas mine are **97·995** and **53·516** respectively. That is to say, my results are in the first case 1/2650, and in the second 1/3350 lower than those of Stas, so that if I admit 1/3000 impurity in my silver this would explain the discrepancy, especially as the value for ammonium and therefore for the atomic weight of nitrogen deduced by Stas from the bromide and from the chloride agree so well:

(18·075 from the chloride),
(18·077 „ bromide),

whilst my values for ammonium do not, but are 18·040 from the bromide and 18·059 from the chloride.

But my silver and my bromine agrée exactly with those of Stas as shown by the weight of silver bromide produced from a given weight of silver. Moreover, the ammonium bromide of Stas seems to have contained some foreign matter, most probably platinum, in vessels of which he largely made his preparations. I found that I could use platinum vessels *for hydrochloric* acid and chlorides but *not for hydrobromic* acid, as the latter attacks platinum when warmed in presence of air in vessels of this material.

The value for ammonium chloride calculated from the data given by Marignac (*Bibl. Univ. Geneve*, 1843, **46**, 367) is **53·486**, but I have

been unable to find how he purified his silver ; but it is obvious that it must have been very pure, as he found that 100 parts of silver were equivalent to 110·343 of potassium bromide, whilst Stas found (as the mean of 14 experiments) 110·345. A further proof of the purity of my silver is given in the paper on the preparation of pure hydrobromic acid above referred to, where my value for this ratio is shown to be 110·349.

I gave some of my silver to Sir W. Crookes when I had no reasons for suspecting any impurity, and he informed me that it was the purest silver he had ever tested spectroscopically, giving fewer lines than a specimen which he had until then regarded as pure, but which on comparison with mine was shown to contain traces of copper.

Every titration performed has been given above as well as every gravimetric determination with the exception of two in which some of the precipitated silver salt was unfortunately lost during transference from the bottle to the filter, these being the silver bromide in IV (a) and the silver chloride in (b). No two determinations were made in exactly the same way throughout, even with those in the same series, but the extreme values differ very little and in no case has any value approached that of Stas.

It is obvious that further determinations of ammonium chloride and also some of ammonium iodide must be made in order to clear up the discrepancies indicated above. Until this has been done it would be premature to discuss the value for the atomic weight of nitrogen as deduced from the equivalent weights of ammonium haloid salts.

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XVI.—*The Nitration of the Three Tolueneazophenols.*

By John Theodore Hewitt and James Henry Lindfield.

Experiments which have been made on the nitration of benzeneazophenol with dilute nitric acid (Hewitt, Trans., 1900, 77, 49) and with the strong acid in sulphuric acid solution (Noelting, *Ber.*, 1887, 20, 2997) lead to the conclusion that in the former case the substance reacts as a phenolic compound, whereas under the latter conditions its behaviour coincides with that which might be expected from a phenylhydrazone of quinone. More recently it has been shown that benzeneazosalicylic acid is quite analogous in its interactions with nitric acid, benzeneazo-*o*-nitrosalicylic acid being obtained on nitration with warm

dilute nitric acid, and *p*-nitrobenzeneazosalicylic acid on nitration with a mixture of concentrated nitric and sulphuric acids (Hewitt and Fox, Trans., 1901, **79**, 49).

In order to obtain further evidence of the generality of this reaction, the three isomeric tolueneazophenols have been nitrated with dilute acid and compared with the substances obtained by coupling toluenediazonium salts with nitrophenol. In each case, identical products were obtained, but as in the case of benzeneazo-*o*-nitrophenol, far better yields were obtained by nitrating the oxyazo-compounds than by coupling the diazotised bases with *o*-nitrophenol.

o-*Tolueneazo*-o-*nitrophenol*, $CH_3 \cdot C_6H_4 \cdot N:N \cdot C_6H_3(NO_2) \cdot OH$

$[CH_3 : N_2 : NO_2 : OH = 2' : 1 : 3 : 4]$.

—A solution of 10·7 grams of *o*-toluidine in 30 grams of concentrated hydrochloric acid and 30 grams of water was thoroughly cooled externally with ice and salt and diazotised with 7·1 grams of sodium nitrite (97 per cent.) dissolved in 15 c.c. of water. The diazotised solution was added to 13·9 grams of *o*-nitrophenol in 100 c.c. of well-cooled methylated spirit containing 27 grams of powdered crystallised sodium acetate. The mixture was allowed to stand overnight and then the alcohol and unattacked *o*-nitrophenol were removed in a current of steam. The azonitrophenol was extracted from the tarry residue by ammonia, precipitated by hydrochloric acid and recrystallised from glacial acetic acid. The yield was extremely small.

The same substance was also obtained in good yield by gently warming 10 grams of finely-powdered *o*-tolueneazophenol with a mixture of 20 c.c. of nitric acid (sp. gr. 1·36) and 60 c.c. of water. The reaction set in at about 40°, the thermometer then rapidly rising to 50°; water was added to reduce the temperature to below 40° and the mixture left for half an hour. The precipitate was collected, washed, and twice recrystallised from glacial acetic acid. The corrected melting point of the substance is 146°; a mixture of the two preparations showed no depression of melting point.

0·2560 gave 36·4 c.c. moist nitrogen at 15° and 765 mm. N = 16·7.

$C_{13}H_{13}O_3N_3$ requires N = 16·3 per cent.

The substance is very soluble in acetone or chloroform, fairly so in acetic acid, benzene, carbon disulphide, or ethyl acetate, but only sparingly so in alcohol or light petroleum.

The *acetyl* derivative, obtained by heating the azophenol (1 part) with fused sodium acetate (1 part) and acetic anhydride (2½ parts) on the water-bath, forms golden-yellow needles after it has been recrystallised from acetic acid.

0·1380 gave 17·1 c.c. moist nitrogen at 26° and 754 mm. N = 13·6.

$C_{15}H_{13}O_4N_3$ requires N = 14·1 per cent.

The substance melts at 108° and dissolves very easily in non-hydroxylic solvents with the exception of light petroleum.

The *benzoyl* derivative, obtained by boiling the substance gently with an equal weight of benzoyl chloride for 1 hour, forms red, prismatic crystals on recrystallisation from benzene. It melted at 118°, softening having previously taken place at about 105°.

0·1300 gave 13·8 c.c. moist nitrogen at 22° and 760 mm. N = 12·0.

$C_{20}H_{15}O_4N_3$ requires N = 12·06 per cent.

In non-hydroxylic solvents, except light petrolenm, the substance dissolves easily although to a less extent than the acetate.

The *ethyl ether* is obtained in very poor yield by the usual means. An idea of the incompleteness of the ethylation is furnished by the details of the following experiment. 0·15 gram of sodium was dissolved in 10 c.c. of 98 per cent. ethyl alcohol, 1·7 gram of *o*-toluneazo-*o*-nitrophenol was then added, and after allowing the mixture to stand for several hours to ensure complete conversion into the sodium salt, an excess (2 grams) of ethyl bromide was added. The tube was heated for 3 hours at 100—110°, and, after cooling, the contents were poured into dilute sodium hydroxide solution and the ethyl ether collected, well washed, and recrystallised from spirit. Only 0·17 gram was obtained, and the unattacked azophenol was easily recovered from the alkaline solution by acidification.* Particular attention has been called to this resistance to alkylation, since the *m*- and *p*-tolueneazo-*o*-nitrophenols give good yields of the ethyl ethers under similar conditions.

0·0962 gave 12·9 c.c. moist nitrogen at 21° and 764 mm. N = 15·3.

$C_{15}H_{15}O_3N_3$ requires N = 14·7 per cent.

The ethyl ether forms orange needles, which melt at 83°; it is fairly soluble in hot ethyl alcohol.

m-*Tolueneazo*-o-*nitrophenol* [$CH_3 : N_2 : NO_2 : OH = 3' : 1 : 3 : 4$] was obtained by both methods, the two preparations individually and when mixed showing the same melting point. It is very necessary to have the *m*-tolueneazophenol in a state of purity before nitration, otherwise tarry mixtures are obtained from which the isolation of a pure substance is difficult, although a fair separation may be effected by dissolving the crude preparation in hot dilute ammonia solution, allowing to cool, filtering, and precipitating the azonitrophenol from the filtrate by means of hydrochloric acid. After several recrystallisations, the substance separates from glacial acetic acid in nearly black, prismatic crystals melting at 127°. By recrystallisation from light petroleum to which a little ethyl acetate has been added to increase the solubility, it can be obtained, however, in fine, yellow

* In the particular experiment described above, 1·1 gram was thus recovered.

needles melting at 128·5°. This alteration of melting point when a different solvent is used is not great, but shows that the removal of the last traces of impurity is no simple matter.

0·1926 gave 26·0 c.c. moist nitrogen at 15° and 760 mm. N = 16·0.
$C_{13}H_{11}O_3N_3$ requires N = 16·3 per cent.

Attempts which were made to introduce acetyl or benzoyl groups in place of the hydrogen of the phenolic hydroxyl group proved abortive, although the *o*- and *p*-isomerides acetylate and benzoylate easily and normally. By long-continued boiling with acetic anhydride and fused sodium acetate, or with benzoyl chloride, oily products were obtained which dissolved in alkali. Even when the azophenol was boiled for 10 minutes with four times its weight of benzoyl chloride, and then allowed to stand in the cold for 3 days, it was found that the crystals which had been deposited from the solution consisted of unaltered azophenol. The great resistance to acylation is remarkable and deserves further attention; perhaps future work may give some clue to the cause.

Alkylation by means of sodium ethoxide and ethyl bromide is, however, readily effected.

The *ethyl ether* was prepared similarly to that of *o*-tolueneazo-*o*-nitrophenol, and a good yield obtained; it separates from alcohol in small, brown crystals which melt at 92°.

0·1065 gave 13·4 c.c. moist nitrogen at 17° and 764 mm. N = 14·7.
$C_{15}H_{15}O_3N_3$ requires N = 14·7 per cent.

p-*Tolueneazo-o-nitrophenol* [$CH_3 : N_2 : NO_2 : OH = 4' : 1 : 3 : 4$] is produced by nitration at about 40°, and, with care, very nearly theoretical yields may be obtained. In one case, 20 grams of *p*-tolueneazophenol yielded 23 grams of dried, crude nitro-compound, which, after recrystallisation from glacial acetic acid, furnished 19 grams of substance melting at 147°. In this case, the constitution of the substance was also settled by comparison with a specimen obtained by coupling benzenediazonium chloride with *o*-nitrophenol. The substance, which forms brown leaflets, is very soluble in benzene, chloroform, or carbon disulphide, and fairly so in acetic acid, acetone, ethyl alcohol, ether, or ethyl acetate, but almost insoluble in light petroleum.

0·1360 gave 0·3035 CO_2 and 0·0640 H_2O. C = 60·2; H = 5·2.
0·1248 „ 17·3 c.c. moist nitrogen at 15° and 768 mm. N = 16·4.
$C_{13}H_{11}O_3N_3$ requires C = 60·6; H = 4·3; N = 16·3 per cent.

The *acetyl* derivative, which was obtained in the usual way, crystallises from acetic acid in small, brown prisms melting at 94°.

0·1173 gave 14·0 c.c. moist nitrogen at 15° and 772 mm. N = 14·2.
$C_{15}H_{13}O_4N_3$ requires N = 14·1 per cent.

The *benzoyl* derivative was prepared by boiling the azophenol with three times its weight of benzoyl chloride for 1 hour. After recrystallisation from a large quantity of spirit, the corrected melting point was found to be 129°.

0·0829 gave 8·9 c.c. moist nitrogen at 29° and 756 mm. N = 11·6.

$C_{20}H_{15}O_4N_3$ requires N = 12·06 per cent.

The substance, which forms small, yellow plates, is easily soluble in solvents of non-hydroxylic character, with the usual exception of light petroleum; it is fairly soluble in acetic acid, but, on the other hand, is only sparingly dissolved by alcohols.

The *ethyl ether* was obtained by the usual method; it separated from alcohol as brownish needles melting at 118°.

0·1405 gave 18·2 c.c. moist nitrogen at 16° and 766 mm. N = 15·1.

$C_{15}H_{15}O_3N_3$ requires N = 14·7 per cent.

Benzeneazo-o-nitrophenyl ethyl ether was prepared for purposes of comparison by heating benzeneazo-*o*-nitrophenol with sodium ethoxide and ethyl bromide. After the usual purification and recrystallisation from spirit, small, brownish needles (frequently arranged in radiating groups) melting at 93° were obtained; the yield was good.

0·1168 gave 16·0 c.c. moist nitrogen at 24° and 753 mm. N = 15·5.

$C_{14}H_{13}O_3N_3$ requires N = 15·5 per cent.

The substance dissolves sparingly in cold ethyl alcohol, fairly easily in benzene or carbon disulphide, and readily in acetone.

The melting points of the substances described in this paper, and also those of the corresponding derivatives of benzeneazo-*o*-nitrophenol, are given in the following table:

	Phenol.	Ethyl ether.	Acetate.	Benzoate.
Benzeneazo-*o*-nitrophenol..	128·5°	93°	120·5°	132°
o-Tolueneazo-*o*-nitrophenol.	146	83	108	118
m-Tolueneazo-*o*-nitrophenol	128·5	92	—	—
p-Tolueneazo-*o*-nitrophenol.	147	116	94	129

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XVII.—*The Bromination of* o-*Oxyazo-compounds and its bearing on their Constitution.*

By John Theodore Hewitt and Henry Ablett Phillips.

The constitution of the *o*-oxyazo-compounds has for some years been a matter of considerable discussion. These, as well as the *p*-derivatives, were at the time of their discovery looked upon as hydroxylic compounds, this view being first of all disputed by Liebermann (*Ber.*, 1883, **16**, 2929). Zincke and Bindewald's discovery that phenylhydrazine reacts with α-naphthaquinone with production of benzeneazo-α-naphthol (*Ber.*, 1884, **17**, 3026), whilst with β-naphthaquinone a substance strongly resembling, although not identical with, benzeneazo-β-naphthol is obtained (*loc. cit.* 3029), led the two latter chemists to look upon *p*-oxyazo-compounds as true azophenols, but upon the *o*-oxyazo-compounds, however, as hydrazones. The possibility then arose that all the substances hitherto regarded as hydroxyl derivatives of azo-compounds might perhaps be hydrazones of quinones.

Many attempts have been made to settle this question. Reduction of alkyl and acyl derivatives has led to somewhat conflicting statements, although, speaking generally, the alkyl derivatives may be regarded as of the true azo-type, that is, they are oxygen ethers both in the ortho- and the para-series (Compare Meldola and Morgan, Trans., 1889, **55**, 608, 609; Witt and Schmidt, *Ber.*, 1892, **25**, 1013; Jacobson, *Annalen*, 1895, **287**, 97, &c.).

Experiments with acyl derivatives have not given such definite results, for whilst in certain cases the scission of these derivatives seems to have been complete and primary amines obtained, from which the conclusion might be drawn that acylation had not taken place with respect to the nitrogen atom, in others acylated amines and aminophenols have been isolated as sole products of the reduction; for example, the acetyl derivative of benzeneazo-*p*-cresol yields only acetanilide and amino-*p*-cresol (Goldschmidt and Brubacher, *Ber.*, 1891, **24**, 2301; compare Meldola, *Phil. Mag.*, 1888, **26**, 403; Meldola and Morgan, Trans., 1889, **55** 114; Meldola and Forster, Trans., 1891, **59**, 710; Meldola, Hawkins, and Burls, Trans., 1893, **63**, 923; Meldola and Hanes, Trans., 1894, **65**, 834). Goldschmidt was indeed inclined to regard the oxyazo-compounds as in all cases quinonehydrazones acylating with respect to a nitrogen atom. The incorrectness of this view was proved by McPherson, who found that *as*-benzoylphenylhydrazine condenses with benzoquinone to form an isomeride of the benzoyl derivative of benzeneazophenol (*Ber.*, 1895, **28**, 2414; *Amer. Chem. J.*, 1899, **22**, 364). Since McPherson's

compound must be acylated with regard to nitrogen, the substance obtained by the benzoylation of benzeneazophenol must have the constitution

$$C_6H_5\cdot N{:}N\cdot C_6H_4\cdot O\cdot CO\cdot C_6H_5.$$

The balance of evidence would seem to be in favour of the acyl as well as the alkyl derivatives being oxygen ethers. Quite recently, however, Möhlau has shown that benzeneazotetramethyldiaminobenzhydryl-α-naphthol,

$$C_6H_5\cdot N{:}N\cdot C_{10}H_5[CH(C_6H_4\cdot N[CH_3]_2)_2]OH,$$

reacts towards acetic anhydride as if it were a quinonehydrazone of the constitution

$$C_6H_5\cdot NH\cdot N{:}C_{10}H_5[CH(C_6H_4\cdot N[CH_3]_2)_2]{:}O,$$

its acetyl derivative giving a practically quantitative yield of acetanilide on reduction (*Ber.*, 1900, **33**, 2858). From this fact and the further observation that other *p*-oxyazo-compounds react readily with tetramethyldiaminobenzhydrol, Möhlau draws the conclusion that the *p*-derivatives must be represented as quinonehydrazones.

In so many instances do compounds undergo change in constitution on alkylation or acylation, that any conclusions drawn from the structure of derivatives must of necessity be doubtful; oxyazo-compounds so easily unite with acids to form additive products of the quinonehydrazone type that the production of a nitrogen ether from an oxyazo-compound might easily take place according to the scheme:

$$NR{:}N\cdot C_{10}H_6\cdot OH \rightarrow \begin{matrix} C_6H_5\cdot CO \\ Cl \end{matrix}\!\!>\!NHR\cdot N{:}C_{10}H_6{:}O \rightarrow C_6H_5\cdot CO\cdot NR\cdot N{:}C_{10}H_6{:}O.$$

On the contrary, the acylation of a quinonehydrazone with regard to oxygen would not be surprising,

$$R\cdot NH\cdot N{:}C_{10}H_6{:}O \rightarrow R\cdot NH\cdot N{:}C_{10}H_6\!<\!\begin{matrix} Cl \\ O\cdot CO\cdot C_6H_5 \end{matrix} \rightarrow R\cdot N{:}N\cdot C_{10}H_6\cdot O\cdot CO\cdot C_6H_5;$$

in fact, it would closely correspond to the conversion of a quinonehydrazone salt into the azophenol through the intermediate stage of the "pseudohydrate" (to use Hantzsch's nomenclature), which in the case of *p*-ethoxybenzeneazophenol, for instance, can be represented in the following manner (compare Auwers, *Ber.*, 1900, **33**, 1302):

$$C_2H_5O\cdot C_6H_4\begin{matrix} \\ Cl \end{matrix}\!\!>\!NH_2\cdot N{:}C_6H_4{:}O \rightarrow C_2H_5O\cdot C_6H_4\cdot NH\cdot N{:}C_6H_4(OH)_2 \rightarrow C_2H_5O\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot OH.$$

It might be expected that physical measurements would give the

most trustworthy results in a case of this sort, and Auwers and Orton's method (*Zeit. physikal. Chem.*, 1896, 21, 355) of determining the molecular weight in non-hydroxylic solvents seemed to give a definite solution to the problem of the constitution of the oxyazo-compounds. Broadly speaking, hydroxylic compounds exhibit association in solutions in benzene and naphthalene, hydrazones, on the contrary, do not; and corresponding to this difference of behaviour, the *p*-oxyazo-compounds give abnormal, whilst the *o*-oxyazo-compounds give normal, values when their molecular weights are determined. The conclusion that the ortho-compounds are quinonehydrazones and the para-compounds true azophenols agrees well with the insolubility of the former and the ready solubility of the latter in cold dilute alkalis.

To obtain chemical evidence in favour of this view, both Auwers and Hewitt (Auwers, *Ber.*, 1900, 33, 1302; Hewitt, Trans., 1900, 77, 99; Hewitt and Aston, *ibid.*, 712, 810; Hewitt and Fox, this vol., 49; Hewitt and Lindfield, *ibid.*, 155) have instituted experiments on the behaviour of oxyazo-compounds with bromine and dilute nitric acid, the conditions chosen being such as to preclude salt formation. In the case of the *p*-oxyazo-compounds, the results obtained were such as were to be expected for true hydroxyl derivatives, and it may be pointed out that in such substitution experiments the group to be detected is not directly attacked but only used to influence the course of substitution; a hydroxyl derivative of azobenzene should be substituted in the phenol nucleus, a quinonephenylhydrazone, on the other hand, in the benzene nucleus of the phenylhydrazine residue.

The results obtained for the *p*-oxyazo-compounds have been fully in accordance with Auwers' view that these substances are true hydroxylic compounds in the free state, and it seemed to be an interesting problem to continue the study of the substitution of oxyazo-compounds in the ortho-series. Using benzeneazo-*p*-cresol as material, it was confidently expected that either the *p*- or the *o*-bromobenzeneazo-*p*-cresol would be obtained on brominating in glacial acetic acid solution in the presence of sodium acetate. On carrying out an experiment it was found that a monobromo-derivative was indeed produced, which, however, on comparison, immediately proved not to be *p*-bromobenzeneazo-*p*-cresol; on synthesising the corresponding *o*-bromobenzeneazo-*p*-cresol, a substance was obtained which differed from the direct bromination product of the azocresol in no very marked degree with regard to melting point. As the purity of any *o*-bromobenzeneazo-compound must depend on the purity of the *o*-bromoaniline diazotised, considerable care must be exercised in the purification of this base. A pure sample of *o*-bromoaniline having been obtained by a process which will be subsequently described, it was diazotised and coupled with alkaline *p*-cresol. A beautiful azo-com-

pound was obtained which in appearance showed a close resemblance to the product of the bromination of benzeneazo-*p*-cresol, but whereas the latter melts at 123°, *o*-bromobenzeneazo-*p*-cresol melts constantly at 116°, and a mixture of the two substances indefinitely at about 90°. Finally, benzeneazobromo-*p*-cresol of the constitution

$$C_6H_5\cdot N{:}N\cdot C_6H_2Br(OH)\cdot CH_3\ [N_2 : OH : Br : CH_3 = 1 : 2 : 3 : 5]$$

was prepared by the coupling of diazotised aniline with *o*-bromo-*p*-cresol and found to be identical with the product we had obtained by the action of bromine on the oxyazo-compound.

Hence benzeneazo-*p*-cresol brominates as if it were a true hydroxylic compound, a result which is at variance with the physical results of Auwers and scarcely agrees with the insolubility of the *o*-oxyazo-compounds in alkalis.

Of such behaviour only three explanations seem possible:

1. That the *o*-oxyazo-compounds are true hydroxylic derivatives.

2. That the *o*-oxyazo-compounds behave in solution in hydrocarbon solvents as quinonehydrazones, but in acetic acid solution on the contrary are hydroxyl derivatives of azo-compounds.

3. That in solution the two forms are in equilibrium, but the oxyazo-form is so much more reactive than the quinonehydrazone that only the derivatives of the first form are obtained in appreciable yield.

Experimental.

*Bromination of Benzeneazo-*p*-cresol.*

5·3 grams of benzeneazo-*p*-cresol and 5 grams of fused sodium acetate are dissolved in 150 c.c. of glacial acetic acid, and 4 grams of bromine dissolved in 5 c.c. of glacial acetic acid are added gradually from a dropping funnel, the temperature being kept below 12°. The brominated compound separates out, being less soluble than the benzeneazocresol. On warming, the substance passed into solution and separated on cooling in long red needles; these were collected, washed, and dried; the corrected melting point is 123°. If the substance is fractionally crystallised, the separations have the same melting point, showing that only one substance results in any appreciable quantity on the bromination of this *o*-oxyazo-compound.

Synthesis from diazotised Aniline and o-*Bromo*-p-*cresol.*—12·5 grams of *o*-bromo-*p*-cresol were dissolved in 8 grams of sodium hydroxide and about 100 c.c. of water. 6·2 grams of aniline were dissolved in 14 c.c. of strong hydrochloric acid and about 100 c.c. of water. The latter solution was treated with 4·8 grams of sodium nitrite dissolved in a little water, the solution of the diazonium salt then being added to that of the bromocresol. Coupling took place with considerably greater

readiness than has been noticed in the case of *o*-dibromophenol and *o*-nitrophenol. After being allowed to stand for 2 hours, the precipitated oxyazo-compound was collected, washed, and extracted with alcohol. The alcoholic solution was allowed to slowly evaporate to dryness; a tarry mass, in which groups of crystals were distributed, was thus obtained. On washing this with cold glacial acetic acid, the tar was dissolved, the crystals being to a certain extent undissolved. The crystals were collected and recrystallised from ether; the substance was then found to melt at 121°. By dissolving it in ether with an equal quantity of the substance obtained by the bromination of benzeneazo-*p*-cresol, and allowing the solution to gradually crystallise, brilliant red needles melting sharply at 123° were obtained. Hence there is no doubt that the two substances are identical, and that in the bromination of benzeneazo-*p*-cresol bromine takes up the ortho-position to the hydroxyl group.

Benzeneazo-*o*-bromo-*p*-cresol is very sparingly soluble in dilute alkalis; it is very soluble in ether, benzene, or hot glacial acetic acid, and fairly so in alcohol, acetone, or light petroleum.

0·2078 gave 0·1362 AgBr. Br = 27·9.

$C_{13}H_{11}ON_2Br$ requires Br = 27·5 per cent.

The *acetyl* derivative, obtained by boiling this compound with three times its weight of acetic anhydride for 2 hours, forms brilliant orange-red needles after recrystallisation from alcohol.

0·1572 gave 11·9 c.c. moist nitrogen at 23° and 750 mm. N = 8·6.

$C_{15}H_{13}O_2N_2Br$ requires N = 8·4 per cent.

The substance is very soluble in acetone or benzene, and is taken up fairly readily by alcohol, acetic acid, or light petroleum. It melts at 83°.

The *benzoyl* derivative was prepared by boiling with an excess of benzoyl chloride. After destruction of the excess of the acid chloride with cold spirit, the substance was collected and recrystallised from boiling spirit, from which it separates in small, yellowish-orange needles.

0·1133 gave 6·8 c.c. moist nitrogen at 20° and 766 mm. N = 6·9.

$C_{20}H_{15}O_2N_2Br$ requires N = 7·1 per cent.

This compound, which melts at 110°, is very soluble in acetone or benzene, fairly so in acetic acid or ether, but only sparingly so in alcohol or light petroleum.

o-Bromobenzeneazo-p-cresol.

As has been explained in the introductory part of the paper, it was at one time thought that this substance was identical with that obtained by the bromination of benzeneazo-*p*-cresol. The first preparation was made with an ordinary specimen of *o*-bromoaniline, and separated as minute, orange crystals melting at 113°. Since the substance yielded unsatisfactory acetyl and benzoyl derivatives, it was concluded that the *o*-bromoaniline used was contaminated with the para-isomeride, and that the *o*-bromooxyazo-compound was likewise mixed with a small quantity of *p*-bromobenzeneazo-*p*-cresol. This supposition proved to be correct, although even when *o*-bromobenzeneazo-*p*-cresol is obtained in a state of purity it does not melt higher than 116°.

As *o*-bromonitrobenzene is never obtained pure commercially, and as *o*-bromoaniline is usually somewhat impure, the following process, which furnishes a pure base, has been devised. Commercial *o*-nitrobromobenzene is reduced in the usual way with tin and hydrochloric acid, and the base driven over with steam after the solution has been rendered alkaline. The crude *o*-bromoaniline is collected, and slightly more than a molecular proportion of acetic anhydride added; the mixture becomes warm, and on dilution with water the acetobromoanilide is precipitated. This is recrystallised from alcohol until it shows a constant melting point (99°); it is then hydrolysed by boiling with aqueous caustic potash, and distilled over in a current of steam. On distillation, the base passes over with a constant boiling point.

If this pure base is dissolved in acid, diazotised, and then coupled with alkaline *p*-cresol, an oxyazo-compound is obtained which crystallises from hot acetic acid in the form of brilliant, dark-red needles melting sharply at 116°. A mixture of this substance with about an equal weight of benzeneazo-*o*-bromo-*p*-cresol melted at about 90°.

0·1606 gave 14 c.c. moist nitrogen at 20° and 762 mm. N = 9·9.
$C_{13}H_{11}ON_2Br$ requires N = 9·6 per cent.

o-Bromobenzeneazo-*p*-cresol dissolves moderately in ether, benzene, acetone, or acetic acid, but is sparingly soluble in alcohol or light petroleum.

The *acetyl* derivative.—When the pure *o*-bromobenzeneazo-*p*-cresol is boiled with acetic anhydride, a well defined compound is obtained, which crystallises in flat, orange-brown needles and melts sharply at 85°.

0·2959 gave 22·8 c.c. moist nitrogen at 20° and 762 mm. N = 8·8.
$C_{15}H_{13}O_2N_2Br$ requires N = 8·4 per cent.

This substance is very soluble in acetone, benzene, or ether, but less so in acetic acid, light petroleum, or alcohol.

The *benzoyl* derivative also crystallises well in small orange plates when prepared from the pure oxyazo-compound; its solubilities resemble those of the acetyl derivative. The substance melts at 106·5°.

0·1166 gave 6·6 c.c. moist nitrogen at 12° and 768 mm. N = 6·75.
$C_{20}H_{15}O_2N_2Br$ requires N = 7·1 per cent.

m-*Bromobenzeneazo*-p-*cresol.*

m-*Bromobenzeneazo*-p-*cresol* was prepared in the usual manner. It forms small, orange-brown needles which melt at 112° and dissolve readily in acetone or benzene, moderately in acetic acid, ether or light petroleum, and only sparingly in cold alcohol.

0·1482 gave 0·2948 CO_2 and 0·0506 H_2O. C = 54·25; H = 3·8.
0·1949 ,, 0·1248 AgBr. Br = 27·3.
$C_{13}H_{11}ON_2Br$ requires C = 53·6; H = 3·8; Br = 27·5 per cent.

These compounds usually give very high values for carbon on analysis, no doubt owing to the presence both of halogen and nitrogen.

The *acetyl* derivative forms small, dark reddish-brown crystals melting at 61—62° which are easily soluble in benzene or ether, and moderately so in other solvents.

0·2085 gave 15·8 c.c. moist nitrogen at 20° and 762 mm. N = 8·7.
$C_{15}H_{13}O_2N_2Br$ requires N = 8·4 per cent.

The *benzoyl* derivative melts at 94° and forms very small, yellow crystals. It dissolves easily in acetone or benzene, moderately in acetic acid or ether, but only sparingly in alcohol or light petroleum.

0·1220 gave 0·2755 CO_2 and 0·0406 H_2O. C = 61·5; H = 4·0.
$C_{20}H_{15}O_2N_2Br$ requires C = 60·6; H = 4·0 per cent.

p-*Bromobenzeneazo*-p-*cresol.*

This substance forms small, orange leaflets melting at 147°. It dissolves fairly in most solvents, but only sparingly in light petroleum.

0·1894 gave 16·4 c.c. moist nitrogen at 20° and 766 mm. N = 9·9.
$C_{13}H_{11}ON_2Br$ requires N = 9·6 per cent.

The *acetyl* derivative forms small, bright orange crystals melting at 123°. It is very soluble in acetone or benzene, and is taken up fairly readily by most other solvents with the exception of light petroleum.

0·2052 gave 15·2 c.c. moist nitrogen at 20° and 762 mm. N = 8·4.
$C_{15}H_{13}O_2N_2Br$ requires N = 8·4 per cent.

The *benzoyl* derivative melts at 112° and separates from solution in very small crystals.

0·1585 gave 10·0 c.c. moist nitrogen at 23° and 753 mm. N = 7·2.
$C_{20}H_{15}O_2N_2Br$ requires N = 7·1 per cent.

Its solubilities, although less than, resemble those of the acetyl derivative.

East London Technical College.

XVIII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. I. Influence of Water, Methyl Alcohol, Ethyl Alcohol,* n-*Propyl Alcohol, and Glycerol on the Rotation of Ethyl Tartrate.*

By T. S. Patterson.

Although at the present time the results of a considerable number of investigations relative to the influence of solvents on the rotation of optically active compounds are available, they seem insufficient to allow of the deduction of any satisfactory generalisations. A few theories have been suggested attributing the phenomena observed, for instance, to difference of solubility of the active substance in the various solvents used or to the formation of chemical combinations of active substance and solution, but no one of these can be said to have met with much success. The work already done appears to be neither sufficiently extensive nor sufficiently systematic. Only in the case of the application of the electrolytic dissociation theory to explain the similarity of the rotations of dilute aqueous solutions of different salts of the same optically active acid or base, do facts and theory correspond, and this, however satisfactory the correspondence may be, is merely a verification of the dissociation theory; it does not help us at all to understand the general effect of solvents on the rotation of optically active substances. For, supposing that the active ion could be obtained free in two different solvents, it would in all probability not have the same rotation in each. Different solvents would presumably have different effects on active ions just as they have on undissociated compounds, and it seems also impossible to explain the behaviour of solutions of optically active substances by assuming varying degrees of electrolytic dissociation in each. This property of causing electrolytic dissociation to any considerable extent is only possessed by a few liquids; in the rest, the physical molecular weight of the solute is the

same as the chemical molecular weight, or it is greater. The question whether the existence of the solute as associated, simple, or dissociated molecules in solution merely depends on some one property of solvents which is developed to a different degree in each, does not yet seem to admit of answer.

However that may be, the theory which asserts that variation of rotation and varying degree of association are causally connected with each other has received a certain amount of credence. In the case of homogeneous compounds, P. F. Frankland (Trans., 1899, 75, 347) has been able to trace a very interesting connection between the abnormal (that is, *à priori* unexpected) rotations often shown by the lower members of homologous series of active compounds and their association factor as calculated by I. Traube's method, and several investigations have been undertaken with the object of ascertaining whether a direct connection could be proved between the rotation and association factors of an optically active substance in solution. The evidence which has thus been collected is unsatisfactory; it perhaps does not absolutely disprove the possibility of the connection sought for, but it leaves plenty of room for doubt as to its probability. The whole question of rotation in solution is one still requiring much careful investigation, and it is the object of this paper, as it will be of succeeding ones, to add at least something to the data on the subject. As the possible connection of association and rotation arises naturally in discussing the experiments detailed below, the short criticism of existing work which is necessary is introduced further on (p. 184).

Ethyl tartrate has been chosen for investigation for the present, since it can be obtained pure without much difficulty, has a sufficiently high rotation to allow of fairly accurate measurement, and is miscible in all proportions with many organic solvents, so that it is possible to draw complete concentration curves, and, finally, has a simple constitution which is fairly well understood. The ethyl tartrate used in this investigation was prepared by boiling tartaric acid with ethyl alcohol (in the proportion of 1 molecule to 4) for some hours. The solution was then cooled and saturated with hydrogen chloride at a low temperature. After an interval of about 12 hours, the gas was removed as far as possible in a vacuum and further expelled, along with excess of alcohol, by heating on a water-bath at a low pressure. A weight of alcohol equal to that previously used was then added and the solution again saturated with hydrogen chloride, which was driven off as before. The residual ethyl tartrate was carefully fractionated several times under about 15 mm. pressure until two successive fractions had identical rotations.

The observed rotation of the product thus prepared was, from the figures given on p. 198, $+9{\cdot}244^\circ$ in a 100 mm. tube, and the specific rota-

tion, therefore, $+7{\cdot}67^{\circ}$. This value agrees well with that found by other investigators who have prepared the ester in the same manner, as the following figures show:

	t.	α_D
Pictet (*Jahresber.*, 1882, 356)	20°	$+9{\cdot}236^{\circ}$
Perkin * (Trans., 1887, 51, 363)	20	9·65
Rodger and Brame (Trans., 1898, 73, 304)	20·1	9·37
Frankland and Patterson (Trans., 1898, 73, 188)	20	9·31
Frankland and McCrae (Trans., 1898, 73, 310)	20	9·323

The optical behaviour of ethyl tartrate in water, methyl alcohol and ethyl alcohol has already been studied by Landolt (*Annalen*, 1877, 189, 311), who, however, in his experiments used an ester having a specific rotation of $+8{\cdot}31^{\circ}$ at 20° and a density 1·1989. That these values do not agree with those of other investigators he assumes to be due to admixture with some inactive impurity, probably alcohol.

The following investigation is somewhat more extensive than his, especially with regard to temperature, it being possible from the figures and curves given to deduce the rotation of ethyl tartrate in each of the solvents dealt with, at any temperature within the limits of the experiments and at any concentration whatever, with fair accuracy.

The instrument used was a Laurent half-shadow polarimeter reading direct to one minute. It is fitted with a large jacket which for use at higher temperatures is filled with hot water and allowed to cool down slowly, observations being made at intervals as the desired temperatures are reached. For readings at 100°, steam is passed through the jacket until the rotation is constant. The liquids to be examined are contained in tubes differing only slightly from the ordinary form. Fig. 1 shows at *A* and *B* two different forms for the ends.

In *A*, a short piece of indiarubber tubing is drawn past the end of the tube so as to project a little beyond the disc, over which it folds to some extent. It is then squeezed against the disc by the brass ring, which is screwed to a corresponding metal collar fitting against the glass flange at the end of the tube.

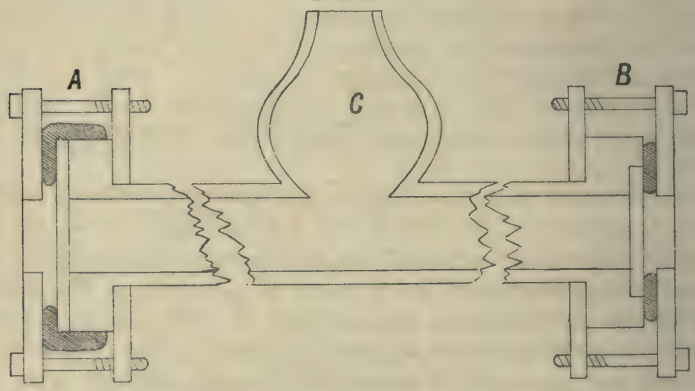
B shows the end of a tube of different form, which was made by Messrs. Schmidt and Haensch, Berlin. The end is flanged as before, but is then ground out so that the disc fits closely into position and flush with the face of the tube. A rubber washer, which has only a very small annular space to cover, is held in position by brass end

* Perkin, in the course of his preparation, dissolved the ester in ether, and treated the solution with anhydrous potassium carbonate, which seems to have effected some slight purification beyond that accomplished by simple distillation.

pieces. This is a very suitable form but much more troublesome to make than the other.

The tubes are also fitted with a lateral tube, *C*, for filling and to allow of expansion of the liquid on heating. This is constricted at the distal end, which is ground flat so as to be about $\frac{1}{4}$ inch in diameter. When the tube has been filled so that no air bubble can be seen on looking through it, the open end of the side piece is closed with a small microscope cover-glass held in position by a rubber band. A small rubber balloon is then slipped over the side piece. This arrangement is found to prevent evaporation very satisfactorily, the density of the solution and the rotation, as will be observed from the figures given, being, in most cases, almost identical before and after the observations at higher temperatures had been made, even when the heating had been carried up to within ten or fifteen degrees of the boiling point of the solvent.

FIG. 1.



The rotations are recorded in the order in which they were observed, so that a comparison of the first and last figures will show to what extent evaporation of the solution has affected the experiments.

The densities, which are all relative to that of water at 4°, were determined by means of Ostwald pyknometers of about 8 c.c. capacity. The error of a determination is probably not more than about three or four units in the fourth place.

Percentage composition throughout this paper is understood to mean grams of active substance per 100 grams of solution.

The expression "after experiment" attached to some of the density data means that the determination was made with the solution taken from the polarimeter tube after the rotation had been observed.

The observed rotations are generally given to three places of decimals, since two successive determinations, each the mean of ten settings of the instrument, agree usually to within a few units in the third

place. The specific rotation is, however, only given to two places of decimals, and in many cases the probable error of a figure for specific rotation may be fairly large, although seldom more than 0·1°, even with dilute solutions.

Nearly all the experimental data in this paper are represented by the curves shown in the different figures, and since these give a comprehensive idea of the results very much more quickly and clearly than the numbers themselves, the latter have been collected and placed at the end of the paper, where reference can easily be made to them when necessary.

The rotation of ethyl tartrate is known to be very sensitive to change of temperature, but although observations have been recorded at 100° and at 20° by various observers and between 12° and 20° by Perkin (Trans., 1887, 51, 368), the rotation does not appear to have been examined at temperatures between 20° and 100°.

The rotation of pure ethyl tartrate at various temperatures was therefore first determined. The figures obtained will be found on p. 198 and the curve obtained from them is shown in Figs. 2, 3, 4, 5, and 6 (the fiducial points being only introduced, however, in Fig. 2), in order that the rotation of the free substance and its solutions may be easily compared.

Ethyl Tartrate in Water.

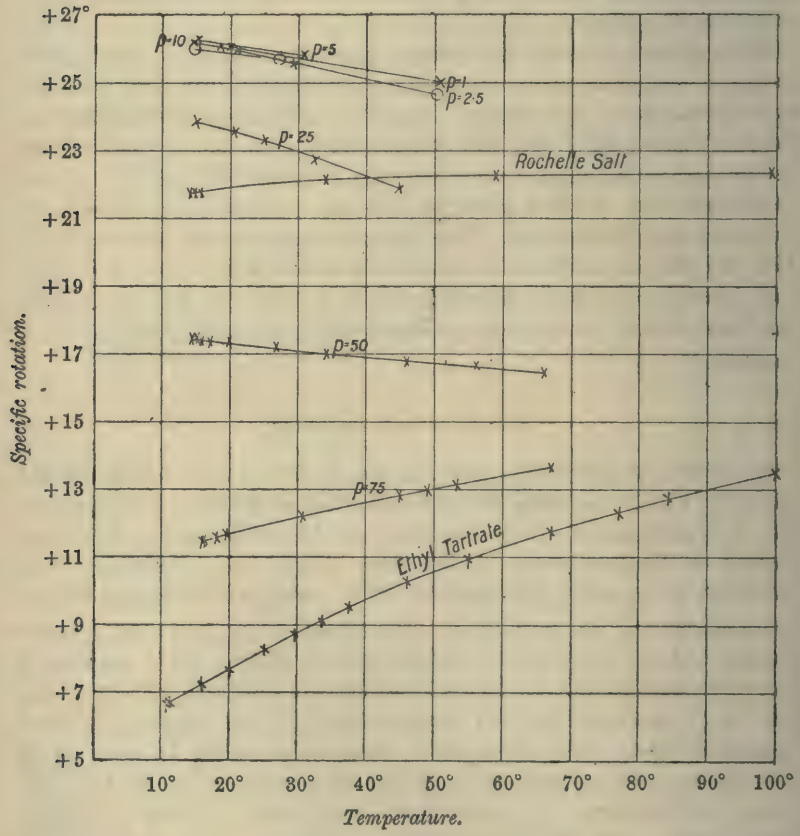
Solutions of percentage composition 1, 2·5, 4·999, 9·994, 24·954, 49·993, 74·99, were made up and examined at various temperatures. The figures obtained will be found on pp. 199—201, and the results are plotted in Fig. 2 as curves which show clearly the behaviour of the rotations of aqueous solutions of ethyl tartrate with regard both to temperature and to concentration, the former being, however, the more obvious. It will be noticed that the curves show a slight amount of irregularity, which is due to the fact that the solutions were heated up first to a comparatively low temperature and the rotation observed, then allowed to cool, and another observation made in order to see whether the heating had produced any permanent effect on the rotation of the solution. The heating was then again carried to a higher temperature than before, another observation made, the solution allowed to cool again, and so on.

The results show that ethyl tartrate is rather more stable in aqueous solution than might have been expected. A 50 per cent. solution may be heated up to 75°, and kept at that temperature for some time without showing, on cooling, any noticeable change in rotation, and this applies to other solutions as well. Only a very slight decrease is noticeable in the rotation of a 5 per cent. solution even after standing

for fifteen days, although a 10 per cent. solution showed a greater change after standing a shorter time.

It is apparent from the curves shown in Fig. 2 that the specific rotation of ethyl tartrate is profoundly modified by solution in water, as was indeed already known from the experiments of Landolt, and from the evidence adduced later on (p. 181) there seems no reason whatever to ascribe this to chemical action of the solvent on the ester.

FIG. 2.—*Specific rotation of aqueous solutions of ethyl tartrate.*



The curve for a solution of $p = 75$ lies considerably above that for the free ester, the specific rotation of the solution at all temperatures for which the curve holds is greater than that of the pure tartrate, and at the same time, it should be carefully noticed, the influence of temperature upon the rotation becomes less marked; the curve for the solution is flatter than that for the ester. Both these influences are more evident in a $p = 50$ solution; the specific rotation is again increased,

the observed rotation for this solution being actually greater than that caused by the same tube filled with pure ethyl tartrate, and the specific rotation of the solution instead of increasing with increase of temperature, exhibits just the opposite behaviour, diminishing slightly. The specific rotation gradually increases with further dilution up to a composition of $p = 10$, when the maximum influence of the solvent appears to be reached, since the value of $[\alpha]^t_D$ is almost identical for solutions of $p = 10$, 5, 2·5, and 1. A 10 per cent. solution may, apparently, so far as rotation is concerned, be regarded as one infinitely dilute, and this maximum influence which the water can exert on the ethyl tartrate molecules dissolved in it, not only increases the rotation of the latter to between three and four times its original value, but produces such a condition in them that increase of temperature causes a diminution in their rotation to nearly the same extent that it produces a rise in the rotation of the free ester, the latter effect being quite as remarkable and interesting as the former.

Landolt's experiments seem to show that the rotation of a solution of ethyl tartrate in water is a linear function of the concentration. This, however, is not borne out by my results, as will be seen by reference to Fig. 8, where, amongst others, the concentration rotation curve for aqueous solutions is shown. The curve is not a straight line, even between $p = 25$ and $p = 100$, but is at first concave to the concentration axis and then convex to it, having a point of inflection at about $p = 50$.

Ethyl Tartrate in Methyl Alcohol.

The figures obtained in the examination of solutions of ethyl tartrate in methyl alcohol for which $p = 5$, 10, 25·01, 56, and 75 will be found on pp. 202—204. They are represented graphically in Fig. 3, which shows the variation in specific rotation with change of temperature. The general appearance of the curves is in all cases similar, but they possibly tend to approach one another somewhat at higher temperatures, although only very slightly, and they preserve also practically the same form as that of the homogeneous ester at any rate up to about 60°. On mixing ethyl tartrate, then, with methyl alcohol, the rotation of the dissolved molecules slowly increases, the influence of the alcohol seeming to reach its maximum when the dilution has been carried to about $p = 10$, since the curve for a $p = 5$ solution coincides almost exactly with that of one for which $p = 10$, though perhaps it is just a little higher.* This variation of rotation with concentration can be seen from Fig. 8. As the dilution increases the rotation also increases

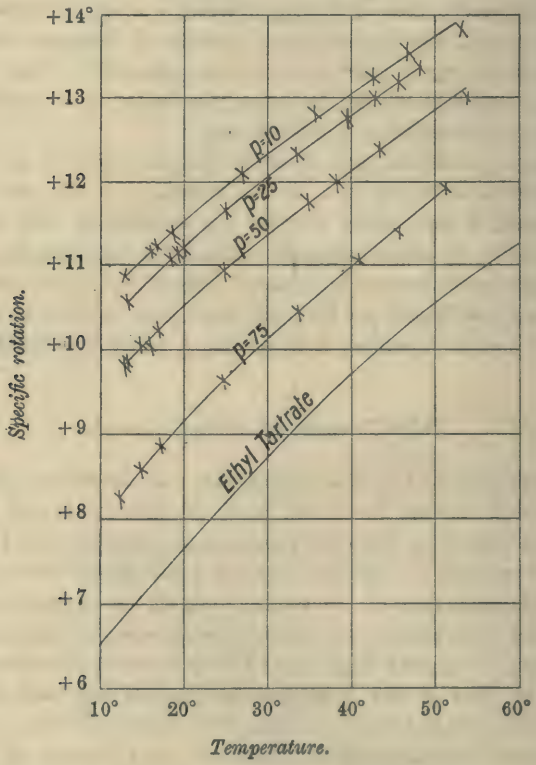
* The curve for $p = 5$ is not shown in the figure, since the fiducial points are apt to be confused with those for a $p = 10$ solution.

to a maximum of about +11·25°, the influence of methyl alcohol being therefore much less than that of water, but in this case, whatever change takes place in the molecule on solution, increase of temperature has the same effect as on the free ester, the rotation increases, whilst in water it diminishes.

Ethyl Tartrate in Ethyl Alcohol.

The solutions examined in the cases of this solvent were of 5, 10·94, 20, 40, and 60·01 per cent. The experimental figures will be found

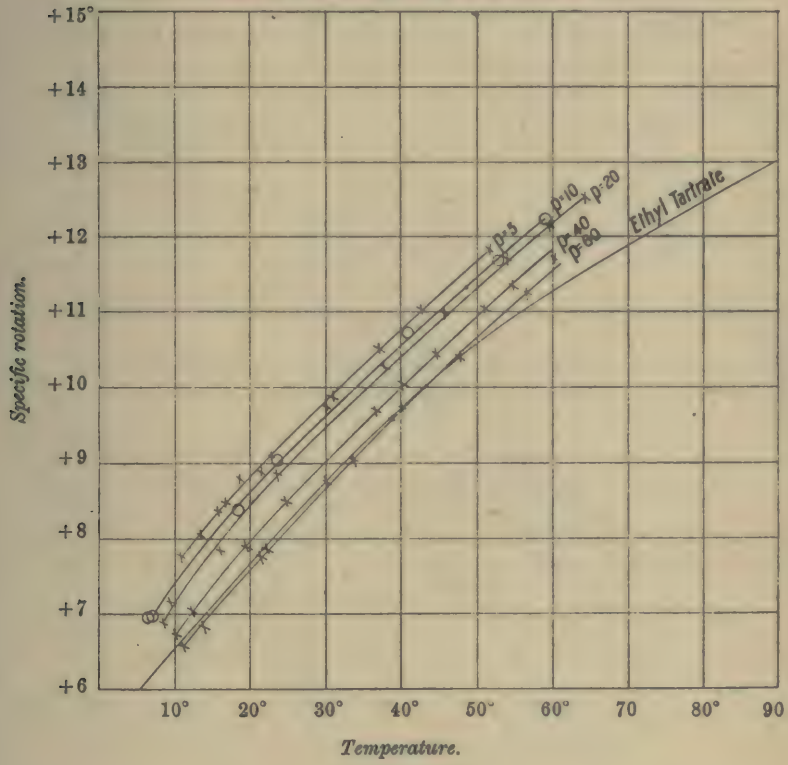
FIG. 3.—*Ethyl tartrate in methyl alcohol.*



on pp. 204—206, and are represented graphically in the accompanying diagram, Fig. 4. It is obvious from the curves obtained that the general behaviour of ethyl tartrate in ethyl alcohol is much the same as in methyl alcohol, although the latter has a markedly greater effect. The specific rotation of dilute solutions is slightly higher than that of the homogeneous substance, but as will be seen from the concentration-rotation curve (Fig. 8), the effect of increasing dilution in this

and the previous case is different. Addition of methyl alcohol to ethyl tartrate causes at first a fairly rapid increase in rotation, which becomes gradually less and less as the dilution increases. Addition of ethyl alcohol, however, causes little or no change in specific rotation until the percentage composition of the solution is about 60. Further addition of alcohol then causes increase of specific rotation, the rate of increase being greater the more dilute the solution becomes. The

FIG. 4.—*Ethyl tartrate in ethyl alcohol.*



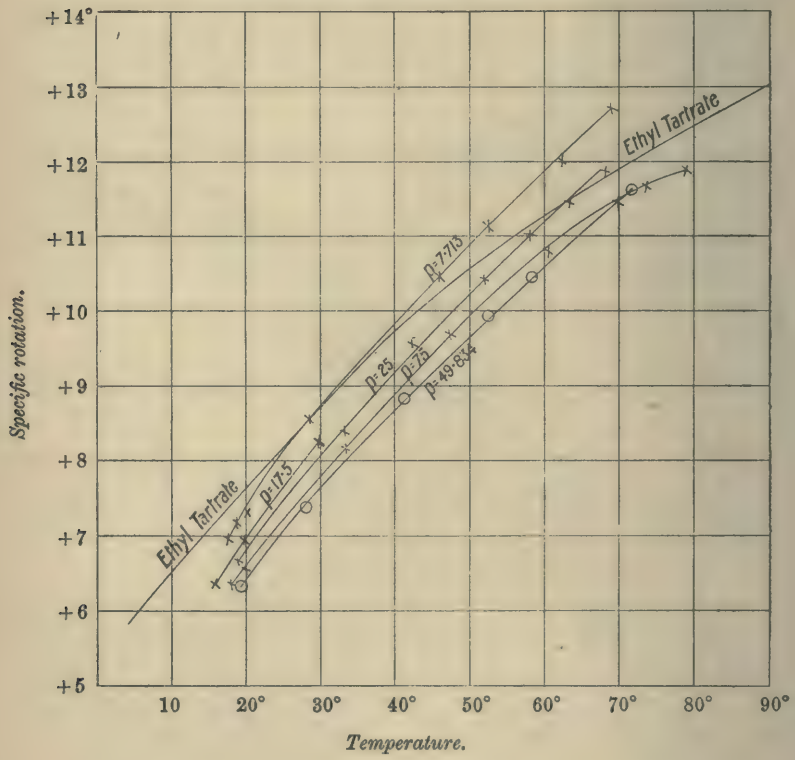
curve obtained is therefore convex to the concentration axis, the maximum effect of the ethyl alcohol being only reached in infinitely dilute solution.

It may be noticed, too, from Fig. 4 that, although the effect of increase of temperature on the ethyl alcoholic solutions and on ethyl tartrate is much the same up to about 50°, it appears to be somewhat different at higher temperatures when the influence of increasing temperature has less effect on the pure ester than on its solutions.

Ethyl Tartrate in n-*Propyl Alcohol.*

The *n*-propyl alcohol which was used in this investigation, although bought as pure, proved to be lævorotatory, but only to so slight an extent that the influence of the impurity is probably completely eliminated by the introduction of a small correction in calculating the specific rotation from the data obtained (see p. 207). 2·5, 5, 7·71,

FIG. 5.—*Ethyl tartrate in* n-*propyl alcohol.*

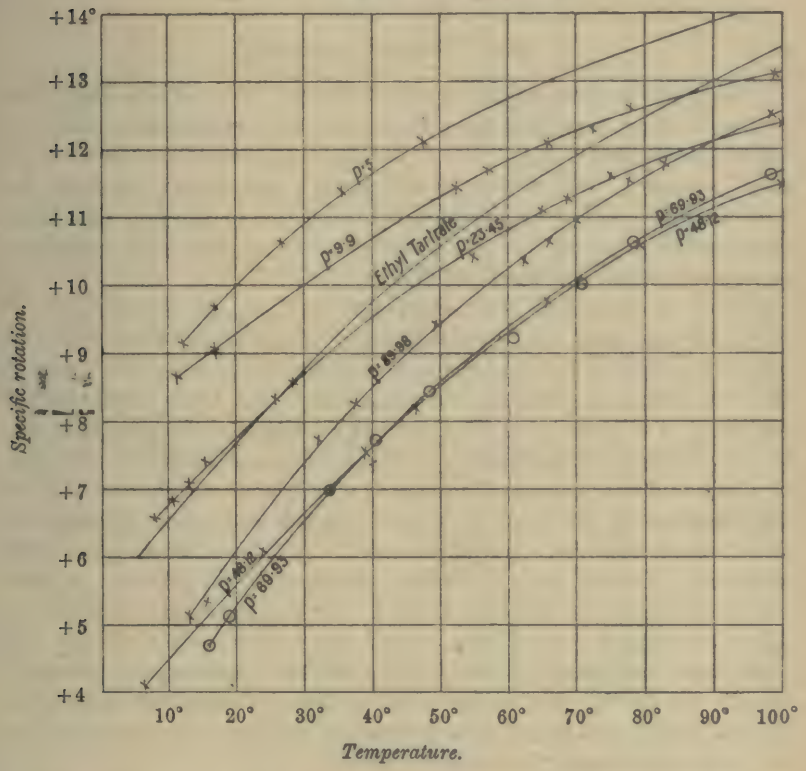


10, 17·5, 25, 37·51, 49·83, and 74·99 per cent. solutions were examined. The experimental numbers will be found on pp. 208—210, and are represented graphically by the curves in Fig. 5. The curves for four of these solutions are, however, omitted in the diagram, as their introduction only tended to cause confusion.

The influence of the other solvents examined is to increase the specific rotation of the dissolved ethyl tartrate, but this effect of the solvent becomes less in passing from water to methyl alcohol and ethyl

alcohol, and in *n*-propyl alcohol becomes such that at low temperatures the rotation is depressed below that of the free ester. The specific rotation of a $p = 75$ solution is at 20° about 1·1° lower than that of pure ethyl tartrate, the addition of alcohol to give a solution of $p = 49{\cdot}83$ diminishing the specific rotation still more. With further dilution, however, the specific rotation gradually rises again, the curve for $p = 25$ lying above those for the concentrations just mentioned, so that when $p = 5$, the specific rotation of the solution is almost as high

FIG. 6.—*Ethyl tartrate in glycerol.*



as that of the free ethyl tartrate. The specific rotation of a solution, however, never seems to quite equal that of the pure ester, and at 20° appears to be constant for any concentration less than $p = 10$, which is apparent from the curve marked "propyl alcohol" in Fig. 8. No solution, therefore, of ethyl tartrate in propyl alcohol below 30° has a rotation as great as that of the pure ester; but it should be noticed that since the rate of variation of specific rotation with variation of temperature is distinctly greater in the solutions, and especially in the

more dilute ones, than in the free ester, this does not hold at temperatures above about 36°.

Another interesting fact to which attention may be drawn is the existence, for any temperature within the limits of these experiments, of a concentration of minimum rotation. Only a few similar cases are known, and in this one the phenomenon is very distinctly marked. As will be seen from Fig. 8, the minimum value of the specific rotation ($+6{\cdot}4°$) occurs (at 20°) when $p=57$. For other temperatures, the concentration at which it occurs is different, being greater the higher the temperature.

Ethyl Tartrate in Glycerol.

The data for these solutions will be found on pp. 211—213. The curves in Fig 6 represent the results obtained in the examination of solutions containing 5, 9·9, 23·45, 48·12, 69·93, and 89·98 per cent. of ethyl tartrate. The curves do not always pass exactly through the experimental points,* the irregularity being due to the fact that these experiments were carried out before the others and with apparatus less suitable than was obtained later.

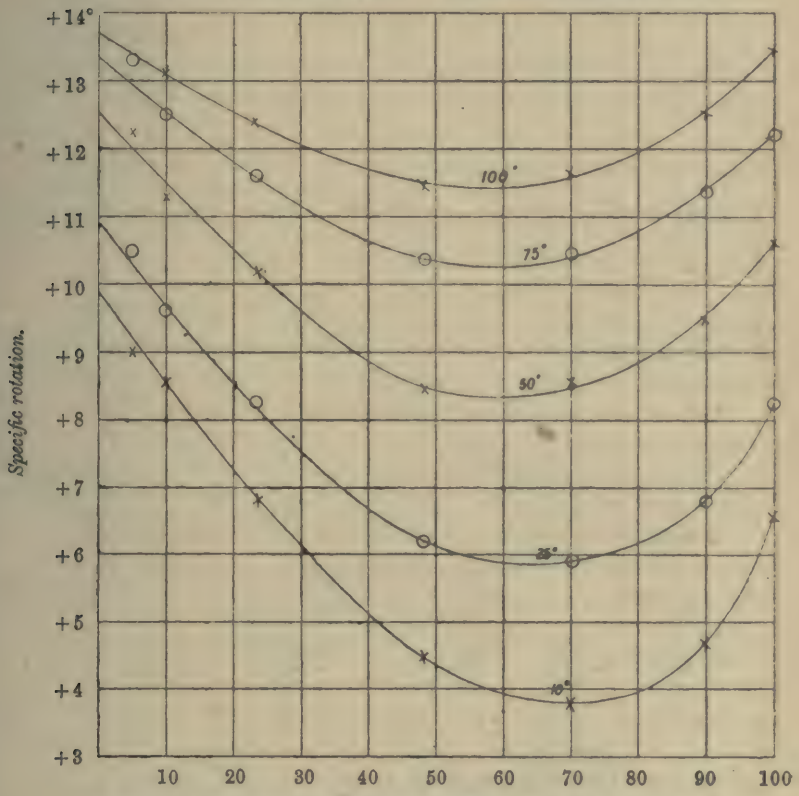
It will be noticed in the first place that the specific rotation of ethyl tartrate may suffer considerable variation by mixture of the ester with glycerol, being either greater or less than, or equal to, that of the free ester, according to the composition and temperature of the solution. The phenomena observed are somewhat similar to those due to the action of *n*-propyl alcohol. The addition of about 10 per cent. of glycerol lowers the specific rotation of the ethyl tartrate at 20° by 1·5°, another 20 per cent. of glycerol causes a further diminution, after which, however, a rapid increase in rotation takes place with increasing dilution, but the effect of glycerol is different in two respects from that of *n*-propyl alcohol. Firstly, the specific rotation of dilute solutions is much higher at low temperatures than that of the ester itself, and secondly, owing to the fact that the temperature coefficient is less for dilute solutions than for the pure ester, the tendency is for the specific rotation of all solutions to sink below that of the free active substance at higher temperatures.

It is obvious that here again we meet with a very good example of solutions of minimum rotation, the phenomenon being perhaps more marked in this than in any case previously observed. A number of concentration-rotation curves for different temperatures are shown in Fig 7, from which it will be seen that the occurrence of the minimum rotation is more pronounced at low temperatures than at higher ones.

* This is particularly the case for a $p=5$ solution at higher temperatures, and is more obvious in the concentration-rotation curves.

The difference between the maximum and minimum rotations at 10° is about 6·2°, whilst at 100° it is only 2·5°, so that with increasing temperature the concentration-rotation curve becomes flatter. The position of the minimum, too, seems to shift to a less concentration with rise of temperature. Thus at 10° the minimum specific rotation

FIG. 7.—*Ethyl tartrate in glycerol. Concentration-rotation curves.*



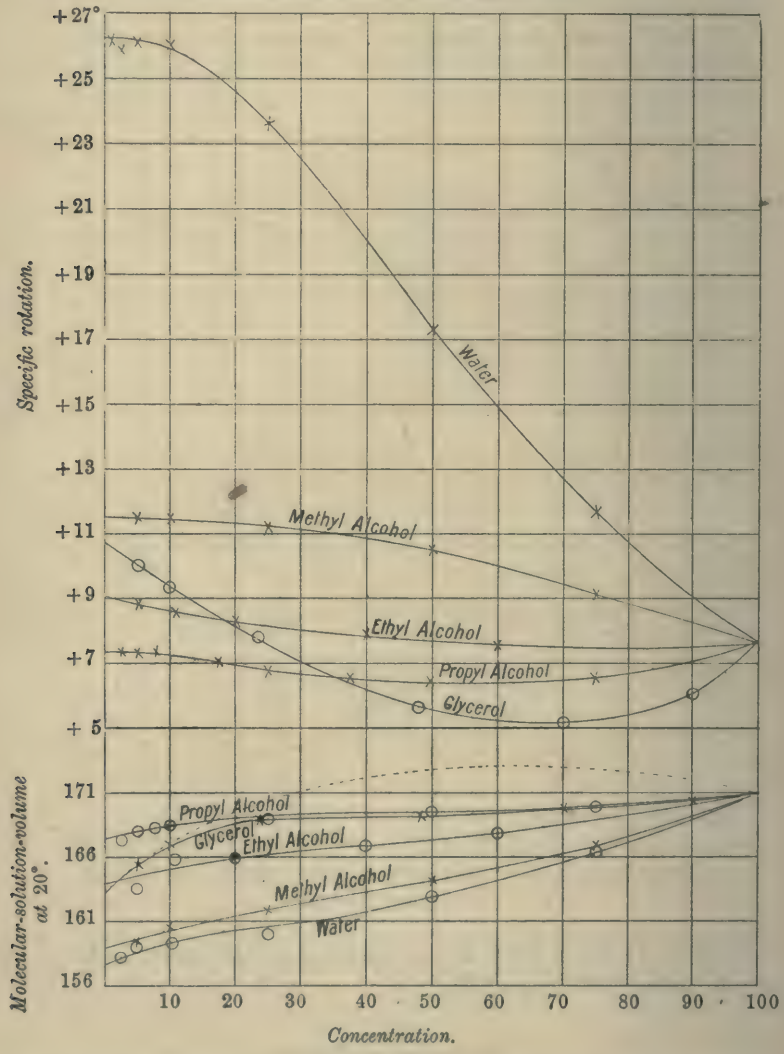
is found at $p = 70$, at 25° it lies at $p = 65$, at 50° at $p = 60$, at 75° about $p = 55$, and at 100° at $p = 53$.

Discussion of Results.

Passing now to a general discussion of these results, since water, methyl alcohol, ethyl alcohol, and *n*-propyl alcohol form part of a homologous series, it is natural to seek, in the first place, for some effect on

the rotation of ethyl tartrate due to their influence and varying in a gradual manner from one solvent to another. It is only in dilute solution that the maximum influence of the solvent can be exerted, and

FIG. 8.—*Relationship of specific rotation and concentration, and of molecular-solution-volume and concentration at 20°.*



in such—for which $p = 10$ or less—a gradual variation may be noticed:

(1) *In the value of the specific rotation,* which decreases as the molecular weight of the solvent increases.

(2) *In the form of the concentration curves*, which gradually changes from the concave for water and methyl alcohol to the slightly convex for ethyl alcohol—with the possibility of a concentration of minimum rotation—and the still more convex curve for *n*-propyl alcohol with a distinct minimum, and, if we include glycerol, to its still more marked minimum and convexity. This is apparent from the curves in Fig. 8.

(3) *In the effect of increase of temperature* upon corresponding solutions. In water, the coefficient is negative, in methyl alcohol it is positive, but perhaps a little less than for the pure ester, in ethyl alcohol it is the same as for the pure ester and for *n*-propyl alcohol distinctly greater, as is apparent from an examination of Figs. 2, 3, 4, and 5.

These three regularities then in the behaviour of solutions of ethyl tartrate in the above solvents may be distinguished; it remains to correlate, if possible, the variation in rotation with some other similarly variable physical property of the dissolved substance, the solvent or the solution.

The results obtained may first be discussed with regard to existing ideas, the most important of which, as already stated, attributes variation of rotation to varying degrees of association of the molecules of the active substance in the different solutions. The variations of the rotation of ethyl tartrate described above are so considerable that if they be really due to this cause one might expect to trace the connection experimentally, and it is noticeable that the rotations stand in the same order as the dissociating power of the solvents used.

That the behaviour of aqueous solutions of ethyl tartrate is remarkable is obvious from the description of it on p. 172; it shows peculiarities which easily suggest the possibility of an exceptional character for such solutions, notably in the remarkably high specific rotation and in the influence of temperature change. It is possible that in aqueous solution ethyl tartrate suffers hydrolysis to ethyl hydrogen tartrate which also has a high rotation (for $c = 2{\cdot}252$ $[\alpha]_D = 21{\cdot}8$ [Fayollat, *Compt. rend.*, 1893, 117, 630]), but this is improbable on account of the fact that no permanent change seems to take place in the solutions on heating; the rotation returns to its original value when the solution cools.

The fact that the molecular rotation of a 10 per cent. aqueous solution of ethyl tartrate is $+53{\cdot}82°$ whilst that of similar solutions of the neutral tartrates is about $+60°$ suggests the possibility of electrolytic dissociation in the former as in the latter, and this, could it be proved to occur in ethyl tartrate solutions, might explain, not only their high rotation, but possibly also the anomalous influence of change of temperature as well. If the rotation of dilute aqueous solutions of ethyl tartrate and the neutral tartrates depends on the same thing,

namely, the existence of the free tartaryl ion in solution, both ought to behave alike with regard to change of temperature, and this appears to afford a means of determining whether the two solutions are similarly constituted.

In order to apply this criterion, a $p = 13{\cdot}68$ solution of Rochelle salt (equivalent to a $p = 10$ solution of ethyl tartrate) was made up and examined in the polarimeter at various temperatures. The experimental figures will be found on p. 214 and are represented by the curve in Fig 2 marked "Rochelle salt." It will be seen that the specific rotation of the Rochelle salt, instead of diminishing, increases somewhat* with rise of temperature, the rate of increase, however, becoming less and less at higher temperatures, so that between 60° and 100° it is almost independent of temperature and it must be concluded that the conditions in the solutions of this salt and ethyl tartrate are not similar.

There remains, however, the possibility of varying degrees of association of the ethyl tartrate in the different solvents used, so in order to ascertain if the complexity of the active substance varies sufficiently with the solvent to account for the rotations observed, the following molecular weight determinations were made.

In water, the cryoscopic method was used with these results:

Calc. mol. wt. = 206.

Weight of substance taken.	Weight of solvent used.	Percentage composition of solution. Grams per 100 grams solution.	Δ.	*M.*
Constant 18·6				
0·2594	9·0578	2·78	0·265°	201
0·3304	11·2638	2·85	0·280	194·8
0·5467	10·2906	5·05	0·495	199·5
0·5940	10·4460	5·38	0·535	197·2
0·8928	9·7404	8·40	0·835	204·2
			Mean	199·3

The molecular weight determinations in methyl, ethyl, and *n*-propyl alcohol were made ebullioscopically.

An apparatus similar (except that it was not graduated for volume measurement) to that recently described by H. N. McCoy (*Amer. Chem. J.*, 1900, **23**, 353) with a thermometer reading direct to twentieths of a degree was used. As a preliminary experiment, the molecular weight of thiocarbanilide was determined in methyl alcohol in which 231·7 instead of the calculated value, 228, was found.

* This had already been shown by Hädrich.

The following are the results:

No.	Weight of ethyl tartrate.	Weight of solvent.	Percentage composition of solution. Grams substance per 100 grams solution.	Δt.	Mol. wt.
Methyl alcohol. Constant 8·8:					
I	1·1972	33·24	3·48	0·144°	220·1
II	1·0654	24·37	4·17	0·175	219·8
III	1·1972	25·18	4·54	0·168	249·0
IV	1·7844	25·02	6·66	0·300	209·2
V	1·7844	17·16	9·42	0·385	237·7
				Mean....	227·2
Ethyl alcohol. Constant 11·7:					
I	1·5225	33·58	4·34	0·245	216·5
II	2·0650	32·72	5·94	0·360	205·1
III	1·5225	21·53	6·61	0·365	226·6
IV	2·0650	19·51	9·57	0·555	223·1
				Mean....	217·8
***n*-Propyl alcohol. Constant = 15·9:**					
I	1·3161	28·544	4·41	0·401	182·8
II	1·7504	22·750	7·14	0·630	194
III	1·6126	19·808	7·53	0·660	196·1
IV	1·8143	22·060	7·60	0·605	216
V	1·5560	17·064	8·36	0·650	221·6
VI	1·7504	16·060	9·83	0·755	229·5
				Mean....	206·6

The distillates from the methyl alcohol determinations were collected and examined in the polarimeter. No rotation could be detected, so that there was probably no volatilisation of ethyl tartrate.

It would appear from the above results that, under the conditions of the experiments, ethyl tartrate exists in these solutions in simple molecules, but obviously any comparison of rotations must be made at the same temperature; it would have little meaning to compare the rotation of ethyl tartrate in water at 0° with those in methyl, ethyl, and propyl alcohols at their respective boiling points, and therefore the question arises whether we may assume that ethyl tartrate in these last three solvents exists in simple molecules at a temperature of, say, 20° as well as at the boiling points. This is, of course, difficult to answer. In some cases it does appear that the molecular weight of a given substance determined at the freezing point in a particular solvent is greater than that obtained in the same solvent at

the boiling point, but if at all, is only slightly greater, and therefore the small amount of association which might be assumed to occur in the above cases at the ordinary temperature scarcely seems to be a sufficient cause to which to attribute the great variation in rotation.

The experimental evidence which has previously been collected on this subject is somewhat unsatisfactory. It is difficult to review it briefly, but a few figures may be given which seem to show the insufficiency of the hypothesis that variation of the rotation of an active substance in different solvents is due to corresponding variation of association.

Freundler (*Ann. Chim. Phys.*, 1895, [vii], 4, 256) has found that, in a number of substances examined by him, when the molecular weight is normal, the rotation is the same or very similar in the free state and in solution, whilst in other cases where the molecular weight is not normal the rotation differs in solution from that of the free active compound. He gives, amongst others, the following examples:

Active substance.	Solvent.	*M.*		$[\alpha]_D$.	
		Calc.	Found	Solution.	Free.
I. Propyl dipropionyltartrate	Ethylene bromide	346	342	+5·4°	+5·5°
II. Propyl diacetyltartrate ...	Benzene	318	277	+1·2	+13·4
,, diphenacetyltartrate	Nitrobenzene	470	378	+14·6	+20·9
,, ,,	Acetic acid	470	377	+27·2	+20·9
III. Methyl tartrate	Benzene	178	411	−8·8	+2·14
Propyl ,, ...	,,	234	306	+20·1	+12·44
,, ,, ...	Ethylene bromide	234	326	−0·6	+12·44

From these figures, Freundler has deduced two "laws," against which, however, it is not difficult to bring objections. It should be noticed, for instance, that propyl diphenacetyltartrate is dissociated to exactly the same extent in nitrobenzene and acetic acid, but whilst in the former solvent the rotation is depressed, in the latter it is raised. Again, propyl tartrate is associated in benzene and in ethylene bromide, the association being accompanied in the former solvent by an *increase* in rotation of about 60 per cent., and in the latter by a *decrease* in rotation of over 100 per cent. on that of the free substance. Surely it may be expected that if these variations in molecular weight and rotation are connected with each other, the effects of association or dissociation should be, at any rate, consistent.

It should be noticed that of the three possibilities, (1) simultaneous normality or abnormality of molecular weight and rotation; (2) abnormal molecular weight with normal rotation; (3) normal molecular

weight with abnormal rotation; the last is much the most important. Of these, (1) may indicate, but does not necessarily prove, a causal connection between variation of rotation and variation of association; (2) does not necessarily disprove such a connection; but (3) if it can be shown that any active substance has normal molecular weight in several different solvents and at the same time very different values for the specific rotation in these solvents, then unless some very good reason can be given to account for this unexpected behaviour, the association hypothesis must be considered disproved. The conditions numbered (3) seem to be met with in the case of ethyl tartrate detailed above, and the following figures taken from a paper by Frankland and Pickard (Trans., 1896, 69, 131) appear to furnish another example.

Methyl dibenzoylglycerate $[\alpha]_D^{15°}$ +26·89°. M = 328.

Molecular weight.		Rotation.	
Percentage composition of solution.	*M.*	Percentage composition of solution.	$[\alpha]_D$.
Solvent: Nitrobenzene.			
3·9	327·1	5·5	20·62
5·3	317·8	17·4	21·72
6·7	315·8		
7·8	322·5		
Solvent: Acetic acid.			
2·0	327·9	4·7	33·27
3·4	304·9	13·6	32·61
5·1	306·4		
5·6	327·6		
7·7	324·9		
16·2	323·7		

Thus the molecular weights are in both cases undoubtedly normal, whilst there is a very considerable difference in the rotations.

Finally, a case cited by Walden (*Zeit. physikal. Chem.*, 1895, 17, 705) may be mentioned.

Ethyl mandelate $[\alpha]_D$ −123·1°.

In acetone.	*In carbon disulphide.*
Molecular weight normal	Molecular weight normal
$[\alpha]_D$ −90°.	$[\alpha]_D$ −180°.

If, therefore, variation of rotation does really depend on variation of association, it will be necessary to attribute a greater influence to an undetectable degree of association than even the constitution of the active substance itself can have.

Of the chemists who seem inclined to adopt this hypothesis, Pope and Peachey (Trans., 1899, 75, 1111) have perhaps pronounced themselves most strongly in its favour, but owing to the fact that they give no direct experimental evidence whatever in support of their views, judgment as to the correctness of their conclusions must be suspended. In the paper in question, these authors seek to base a method of discriminating between racemic and non-racemic liquids, which consists in ascertaining whether the value of the rotation of one of the forms of an optically active substance changes when dissolved in an inactive mixture of both forms. If the externally compensated substance be racemic, then, according to these authors, the molecular condition of the active form will alter when dissolved in it, this being the case "since an optically active substance *necessarily** has different rotation constants according as it is associated to different degrees," and therefore, although the evidence is "rather meagre," "we must expect to find that the specific rotatory power of substances having high association factors in the pure liquid state varies considerably with change of solvent and of concentration, whilst those substances having in the pure liquid state association factors approximating to unity would in solution have specific rotatory powers but slightly dependent on the solvent and the concentration."

The authors assume that the association factor of *l*-tetrahydroquinaldine is about 1·5—which may or may not be the case—and then show (p. 1116) that when dissolved in different media this substance gives various values for $[\alpha]_D$ lying between $-45{\cdot}9°$ and $-97{\cdot}6°$; "the specific rotatory power of the base in piperidine solution is less than one-half of what it is in carbon tetrachloride solution. These large variations in specific rotatory power with change of solvent *can only be attributed* to differences in the degree of association of the base in the various solutions."

Considering that molecular weight determinations could have been carried out in at least seven of the nine solvents (excluding acetic acid) used, it does not seem necessary to resort to the indirect "corroborative evidence" which the authors adduce, namely, that the specific rotation of *l*-tetrahydroquinaldine is the same in the free state and when dissolved in its lower homologue, tetrahydroquinoline, this being the case (p. 1117) "because the association factor remains almost unchanged."

* In this and the other passages quoted, the italics do not occur in the original.

l-Tetrahydroquinaldine was then dissolved in the externally compensated base. If, in the latter, "the two antipodes are not quite mutually indifferent, the association factor would change on admixture and lævotetrahydroquinaldine *could not have* the same specific rotatory power when dissolved in the externally compensated base as solvent as when solvent-free."

The rotation in these two conditions, it appears, is identical, and this proves "in the most conclusive manner possible," that the externally compensated base is not racemic.

On the other hand, "the determinations of the densities and refraction constants of lævo- and externally compensated tetrahydroquinaldine indicate with great probability that the association factor is the same in both." Is not this evidence quite as conclusive as, or even more conclusive than, that derived from the rotation data, involving as it does fewer purely arbitrary assumptions? It will be seen at once that Pope and Peachey's statements do not rest on any solid foundation, and their paper has been referred to here because the results of the experiments detailed in the present communication seem to be absolutely at variance with the fundamental assumptions of the authors. If, as they assume, substances which from their nature should have high association factors exhibit very different rotatory powers as the solvent is changed, then it follows, as they admit (p. 1112), that "those which should be nearly monomolecular [must] vary but slightly in specific rotatory power in like circumstances."

Pope and Peachey depend for evidence as to the association of tetrahydroquinaldine on some data given by Traube regarding aniline, pyridine, quinoline, and piperidine. Now according to Traube's method of calculation, ethyl tartrate is a unimolecular substance. Its molecular volume at 15° (170·1) agrees closely with the calculated value (171·3 [Frankland, Trans., 1899, 75, 349]), and therefore the value of its specific rotation in different solvents should be very similar. As a matter of fact, however, the specific rotation of a 5 per cent. aqueous solution (+26°) is just three and a half times as great as that of a 5 per cent. *n*-propyl alcohol solution (+7·4°), whilst there is no reason to suppose that any marked difference in degree of association exists in the two solvents.

Although, therefore, it may be still premature to deny the connection between association and rotation, that hypothesis can scarcely be considered strong enough to discourage an attempt to trace the phenomena of rotation in solution to some other cause, to some physical property of solvents which, *à priori*, might be expected to exercise a marked influence on any substance dissolved in them.

The Relationship between the Rotation of Active Substances in Solution and the Internal Pressure of the Solvent.

Are we acquainted with such a property of solvents as this? The few necessary conditions which it must fulfil are these:

(1). There must be some reasonable probability of its connection with rotation.

(2). It must be capable of approximate or relative measurement.

(3). In order to account for the very considerable changes which occur in the rotation, it must vary in different solvents between wide limits.

These requirements seem to be met by that property of liquids known as the "internal pressure," which often assumes enormous proportions and which varies very greatly in different liquids.

It was in the hope of connecting this pressure with rotation that the present investigation was commenced, but the idea appears to have been originally suggested by Tammann, and is attributed to him by Siertsema (compare Abstr., 1900, **78**, ii, 329). The latter author has determined the influence of external pressure on the rotation of solutions of sucrose, and if external pressure is capable of influencing rotation, the fact is an encouragement to the investigation of the effect of internal pressure in this direction.

The values given by the various authorities for the internal pressure of any given liquid are often very different. According to Tammann, its value in water at 0° is about 22,000 atmospheres, whilst in ether at the boiling point it is nearly 2,500 atmospheres; according to Ostwald, the values are about half the above, the figures of other investigators being again different, but the relation amongst themselves of the figures of one authority for a number of liquids is generally much the same as that of the figures given by another.

In order to see how this pressure * would act, we can suppose a molecule of ethyl tartrate taken from amongst a large number of similar molecules and placed amongst a large number of water molecules. The pressure on the molecule changes then from the value which it has in ethyl tartrate to that which it has in water. The first effect which we are accustomed to associate with change of pressure is change of volume. The volume of the ethyl tartrate molecule will change, and although, according to Tammann (*Zeit. physikal. Chem.*, 1896, **21**, 529) this change of volume is the sum of several changes, we may assume as a first approximation that in dilute

* Although the word pressure is used throughout for the sake of clearness, it is without any intention of instituting a too strict analogy between this property and ordinary hydrostatic pressure.

solution the change in volume is suffered entirely by the dissolved substance. Traube, in his recent work on molecular solution volume, assumes that it is suffered by the solvent, but his grounds for doing so are not completely convincing. It seems somewhat unwarrantable to suppose that when one molecule of ethyl tartrate is dissolved in, say, one hundred molecules of water, the latter should be altered and not the former. At any rate, a volume change does take place on solution, which we seem at liberty to attribute to the ethyl tartrate, and which we may regard in the meantime as a measure of the change of internal pressure.

If now the molecule of ethyl tartrate were quite regular, this change of pressure would probably produce no corresponding change in rotation. It is, however, assumed to be asymmetric, and consequently when the volume alters so also will the shape. But it is the shape, or something corresponding to the shape, of the molecule that conditions the value of the rotation, and therefore with alteration of volume a corresponding alteration of rotation may be expected.

A mechanical conception of the process is not difficult to form, but the simplest illustration (suggested by Dr. Stroud) is afforded by a figure (say a cube) cut out of a substance whose elasticities are different along the three axes. Such a figure, subjected to hydrostatic pressure, would alter, not only in volume, but in shape as well. This change in asymmetry of an active molecule will bear some proportion to the change in rotation, and it should also bear a relationship to the change in volume, and we may therefore expect to find a connection between the rotation of a substance dissolved in various media and its volume in the same media. The data for calculating the change in volume of ethyl tartrate when dissolved in several solvents are given by the density determinations, so without troubling in the meantime about its cause, we may turn to a comparison of the change in volume with that in specific rotation.

The volume of a gram-molecule of a compound in solution may be calculated from the following formula which has recently been used by Traube:

$$M.S.V.\ (\text{molecular-solution-volume}) = \frac{M+S}{d} - \frac{S}{\delta}.$$

Where M = molecular weight of dissolved substance.

S = weight of solvent associated with 1 gram-molecule of dissolved substance.

d = density of solution.

δ = density of solvent.

If the solution is one of percentage composition p, then M grams of sub-

stance are associated with $\frac{M(100-p)}{p}$ grams solvent, that is,

$$S=\frac{M(100-p)}{p},$$

and, substituting this value of S in the above equation, we find

$$M.S.V.=\frac{M}{p}\left\{\frac{100}{d}-\frac{100-p}{\delta}\right\}.$$

The figures which have been calculated by means of this formula will be found on pp. 214—215, and in Fig. 8 these values of molecular-solution-volume at 20° are plotted relatively to concentration, and below the corresponding concentration-rotation curves for the same temperature. It is evident, in the first place, that the values obtained for molecular-solution-volume in dilute solutions are somewhat uncertain, this being due to the difficulty of carrying out the density determinations with sufficient accuracy, the effect of a slight error being great in dilute solutions, as is apparent from an examination of the formula used in the calculation. It is therefore rather difficult to determine how the most probable curve should be drawn in each case from the experimental data. The curves for water and methyl alcohol are not very satisfactory for $p<10$, whilst that for ethyl alcohol is the least satisfactory of all; it has been drawn, however, as nearly as possible between the values for $p=5$ and $p=10{\cdot}94$.

The ethyl tartrate molecule evidently undergoes a very considerable change in volume on solution in a large quantity of water. At infinite dilution, the molecular-solution-volume seems to be about 157·5 c.c. at 20°, that of the free ester being 170·9 c.c. In methyl alcohol, the change in volume is also considerable but not so great as in the case of water, the value at infinite dilution being about 159·3 c.c. In ethyl alcohol, the volume is 164 c.c. whilst in *n*-propyl alcohol it is 167·7 c.c.

If now the corresponding concentration-rotation curves are examined, it will be noticed that the values of the rotations at infinite dilution stand in the inverse order, and although the rotations do not seem to be quantitatively related to the values of the molecular-solution-volume, there may be a qualitative relationship.

There can be little doubt that the order of the values of molecular-solution-volume at infinite dilution in the above four cases is correct, although the values themselves are a little uncertain, but it is more difficult to say whether the rotation of ethyl tartrate in glycerol can be similarly explained by the value of its molecular-solution-volume in that solvent. As has already been remarked, the accurate determination of molecular-solution-volume becomes more and more difficult as the dilution of the solution increases, and it may be that the curve

drawn in Fig. 8 for glycerol is not correct and that the molecular-solution-volume at infinite dilution is greater than that of ethyl tartrate in ethyl alcohol. Nevertheless, the curve obtained from the experimental figures is so regular as to be some guarantee of its accuracy, and assuming it to be correct the molecular-solution-volume of ethyl tartrate in glycerol at infinite dilution has a value between those found in ethyl alcohol and methyl alcohol, namely, 163·3, and, in agreement with this, the rotation of glycerol is greater than in ethyl alcohol and less than in methyl alcohol. At infinite dilution, therefore, the order of the rotations and molecular-solution-volumes correspond inversely, a small volume being associated with a high rotation, as is apparent from the following table:

Solvent.	M.S.V. (infinite dilution).	$[\alpha]_D$ (infinite dilution).	Change in α_D due to solution.
Water	157·7	26·15°	18·49°
Methyl alcohol	159·3	11·50	3·84
Glycerol	163·3	10·57	2·91
Ethyl alcohol	164	9·13	1·47
n-Propyl alcohol	167·5	7·40	−0·26

The parallelism of these figures is, as a first approximation and in a qualitative sense, fairly satisfactory, but if this relationship is not merely accidental, that is, if variation in molecular-solution-volume does really determine variation in specific rotation, then we may expect to find a connection, not only at infinite dilution, but under all circumstances. That is to say, the curves for rotation should correspond throughout with the true curve for molecular-solution-volume.

Now it will be seen in Fig. 8 that the molecular-solution-volume curves for ethyl tartrate in water, methyl alcohol, ethyl alcohol, and *n*-propyl alcohol are all, in fact, of much the same form, they show a gradation of a similar order to that found in the rotation curves, and this connection between rotation and volume becomes much more striking when glycerol is also taken into account, because its behaviour differs markedly from that of the other solvents; it presents something of the character of an exception, and if an exceptional variation in rotation is accompanied by exceptional variation in molecular-solution-volume, the suggested correlation of these two phenomena becomes more probable. The concentration-rotation curve for this last solvent is, as has already been mentioned, a remarkable one. At 20°, the rotation at infinite dilution is +10·6°. As the concentration increases, the rotation diminishes much more rapidly than in the three other alcohols, and corresponding with this the volume increases much more

rapidly between $p = 0$ and $p = 20$, and in the meantime this qualitative relationship is sufficient. It can scarcely be expected that the molecular-solution-volume curves should cut one another at exactly the same concentrations as those at which the corresponding rotation curves intersect. It might be possible to trace this close connection if the *true* curves for molecular-solution-volume were known; the curves drawn are, however, only approximations, and in all probability not very satisfactory ones. All the contraction on solution has been assumed to take place in the ethyl tartrate. Probably even in a $p = 5$ solution the error thus committed is considerable, and in a $p = 20$ solution it must certainly be great. In the diagrams, however, this volume change is assumed to take place, for all concentrations, in the ethyl tartrate only, which is certainly incorrect.

In reality, the total volume change consists of at least two changes, one in the solute and one in the solvent, but, what is of the greatest importance here, it is not possible to separate it into these two or more simple changes. The curves on the lower part of Fig. 8 are therefore not correct, although they can probably still give some indication as to the actual behaviour of the substances examined. This (the merely approximate nature of the curves) explains why solutions having the same specific rotation need not necessarily show the same molecular-solution-volume for the dissolved ethyl tartrate. The volume of the tartrate may really be the same in two different solutions whilst the volume change in the solvents is not the same. For instance, a $p = 25$ solution in glycerol has the same rotation ($+7{\cdot}6°$) as a $p = 55$ solution in ethyl alcohol, although the corresponding volumes are not the same, being for the former 169 c.c. and for the latter 167·5 c.c. It is evident that in this case a greater volume change is likely to have taken place in the ethyl alcohol of the latter solution than in the glycerol of the former, both of these changes, however, from the method of calculation, being ascribed to the ethyl tartrate alone.

Such a connection as this between molecular-solution-volume and rotation appears to render possible a rational explanation of that very interesting phenomenon, the occurrence of a minimum rotation of ethyl tartrate dissolved in glycerol or *n*-propyl alcohol. For if rotation is really dependent on molecular-solution-volume and in glycerol solution at 20° the minimum rotation occurs when $p = 65$, then it follows that the molecular-solution-volume for the same temperature should be a maximum at that concentration. Now the molecular-solution-volume curve for glycerol rises rapidly with increasing concentration up to about $p = 25$, after which the increase is much more gradual; but at about $p = 25$ it is probable that the glycerol also suffers considerable change in volume and if this be contraction it will

counteract the effect of expansion in the ethyl tartrate. That is to say, the ethyl tartrate may really continue to expand with increasing concentration, the state of affairs not being represented by the full line in the figure but rather by the broken one, until at about $p = 65$ a maximum volume of about 173 c.c. is reached, the volume then again diminishing rapidly to 171 c.c. when $p = 100$. This assumes the possibility of a value greater than normal for ethyl tartrate in solution, which is, however, surely as possible as one less than the normal.

So far it would seem that the assumption of a relationship between molecular-solution-volume and rotation is at least worthy of consideration, but there are considerable difficulties to be overcome before the connection can be regarded as proved. One of these is met with in the fact that in *n*-propyl alcohol, although the molecular-solution-volume at infinite dilution is only 167·1, the rotation is lower than that of the pure ester by 0·26° instead of being higher. The discrepancy is not very great, and an explanation can scarcely be expected until more data have been obtained.

Another difficulty occurs when the influence of temperature change upon the rotation of these solutions is considered. Except in one case—solution in water—increase of temperature causes increase of rotation. But increase of temperature also causes increase of molecular-solution-volume and therefore ought to be attended by decrease of rotation.

We have here a direct contradiction, but the following consideration will show that it is not inexplicable. Let us take the case of free ethyl tartrate, whose rotation, as is well known, increases rapidly with rise of temperature. Imagine one particular molecule, A, in the liquid kept at a definite temperature, T, whilst all the others are heated to a higher temperature. The pressure on the molecule A will decrease, its volume will increase, and its rotation should also decrease ; that is to say, the molecule becomes less asymmetric.

Now let the molecule A be also heated to the higher temperature. The effect will be expansion of the molecule A against a certain pressure—certain forces—resulting in another increase of volume. In this second case, however, the proximate cause of change of volume is not the same as before—the effort comes from within the molecule, the change is not due to variation in the properties of surrounding molecules—and now the expansion may take place in such a way that the molecule becomes more asymmetric again, and since we know in general that a slight change in the temperature of a liquid or solid will produce a much greater alteration of volume than an enormous change of pressure can bring about, the second of the operations just mentioned will probably have a greater effect than the first on the rotation of the molecule A, so that the net result is an increased rotation.

The same volume might be arrived at either by heating or by diminution of pressure alone, but the shape, that is, the asymmetry, of the molecule would not be similar in each case. The asymmetry of the molecule then depends on temperature and pressure—or something analogous to pressure—but it is only constant for definite values of both variables; the asymmetry is not so simply conditioned as the volume.

If this is admitted, then the simultaneous increase of rotation and volume presents no difficulty either in the case of solution in the alcohols or in water, although in the latter case the rotation in dilute solutions (anything less than $p=55$) decreases with increase of temperature. In dilute aqueous solution, where the internal pressure is great, the asymmetry of the ethyl tartrate molecule has become such that the effect of increasing temperature is to produce a less asymmetric molecule. Under a low pressure (solutions in the alcohols) effort from within the molecule produces greater asymmetry; under a high pressure,* it produces a less asymmetry, and consequently between these extremes there may be a pressure under which the molecule of ethyl tartrate has an asymmetry practically unaltered by heating, increase of temperature causing expansion of the molecule certainly, the shape, however, remaining always the same. This particular case appears to be found in an aqueous solution for which $p=55$. The rotation of such a solution is practically insensitive to temperature. In this connection, it should also be noticed that the ethyl tartrate molecule appears to be most sensitive to temperature in those solvents in which its molecular-solution-volume is greatest, which fact is in agreement with the above considerations. In dilute glycerol solutions, the sensitiveness of ethyl tartrate is probably slightly less than that of the free ester, whilst in methyl and ethyl alcohols it is practically the same as that of the free ester. In *n*-propyl alcohol, however, it is rather greater. This corresponds with what has been suggested above; the greatest sensitiveness is shown in that solvent in which molecular-solution-volume is high, that is, in *n*-propyl alcohol.

It is obvious, however, that here again we meet with difficulties, for the molecular-solution-volume of the ethyl tartrate in an insensitive aqueous solution (that is, of $p=55$) is about 163 c.c., which is higher than the volume in infinitely dilute methyl alcoholic solution (159·3 c.c.), and therefore the rotation of dilute solutions in the latter solvent ought also to decrease with increasing temperature, which, of course, is not the case. We must remember, however, that it is not possible to tell what the true molecular-solution-volume of ethyl tartrate in 55

* Always in this particular case of ethyl tartrate, of course. With some other molecule of different asymmetry, the phenomena might be reversed.

per cent. aqueous solution really is, and consequently must be content in the meantime with the indications already pointed out.

This relationship of rotation and molecular-solution-volume has been first discussed because the figures necessary for the calculation of both these quantities may be directly obtained from the data collected in this investigation. As already remarked, however, the volume change accompanying solution is probably more complicated than has been assumed, and it is worth while to try to trace the cause of variation in rotation still further back, namely, to that property of liquids which has been supposed to be the cause of variation in volume, the internal pressure. It may be that the variations in volume due to solution are not directly proportional to variation of internal pressure whilst the variations of rotation are, and that therefore there may be a closer and more obvious connection in the latter case than in the former. Barmwater (*Zeit. physikal. Chem.*, 1899, **28**, 124) has calculated this quantity for a number of substances, and Traube has suggested a method of calculation based on his work on molecular-solution-volume, whilst others have been proposed by van der Waals, Stefan and Tammann.

The choice of a particular set of figures would involve a critical discussion of the various methods of calculation, and this we may avoid by considering, instead of the pressure, that which Brühl (*Zeit. physikal. Chem.*, 1899, **30**, 43) calls the medial energy or heat of disgregation of a liquid, because it is from this quantity that Stefan and Tammann both derive—although by slightly different reasoning—their figures for internal pressure.

The heat of disgregation is calculated from the formula

$$D = H - \frac{p(V - V_1)}{E},$$

where D = heat of disgregation, H = heat of vaporisation, p = vapour pressure, V = volume of 1 gram of vapour, V_1 = volume of 1 gram of liquid, E = mechanical equivalent, which, since we may set

$$p(V - V_1) = \frac{RT}{M},$$

where M = mol. wt. of substance, reduces to

$$D = \frac{MH - 2T}{M}.$$

The heat of disgregation therefore represents the amount of energy necessary to overcome the internal forces of a liquid, and to separate its particles from each other at any particular temperature and pressure.

By calculation from the above formula, the following figures are obtained.

Solvent ($t=0°$).	D.	Δ.	$[\alpha]^{0°}_{D}$.	Δ.
Water	575·9	303·8	+26·5° ($p=10$)	17·0
Methyl alcohol	272·1	48·7	9·5 ($p=10$)	3·3
Ethyl alcohol	223·4		6·2 ($p=5$)	

It will be noticed that here the differences in rotation and heat of disgregation are nearly proportional to each other.

By making the calculations for a higher temperature, *n*-propyl alcohol may also be included in the table. Its heat of vaporisation has only been determined at the boiling point, and has been found to be 166° (cal.). By assuming that it varies in the same manner with temperature as those of methyl and ethyl alcohols, the value at 60° can be approximately obtained. From the number thus deduced, the heat of disgregation in the following table has been calculated:

Solvent ($t=60°$).	D.	Δ.	$[\alpha]^{60°}_{D}$.	Δ.
Water	523·1	274·5	+24° ($p=10$)	9·9
Methyl alcohol	248·6	47·0	14·1 ($p=10$)	1·8
Ethyl alcohol	201·6	26·4	12·3 ($p=10$)	0·5
n-Propyl alcohol	175·2		11·8 ($p=5$)	

These figures are also in fairly close agreement with each other; the rotation in the different solvents appears to decrease in much the same proportion as the heat of disgregation. Such an agreement may of course, be merely accidental, and the examination of several other series of solvents will be required to determine the point, but the figures are certainly striking. Plotted on a system of coordinates, the one property is seen to vary almost linearly with the other. It is not necessary, however, to enter into any further discussion regarding this relationship, for nearly everything that could have been said here has been said for molecular-solution-volume, and applies almost equally to both.

It would appear, then, that molecular-solution-volume, heat of disgregation and rotation have some connection with each other, and in the paper already mentioned Brühl shows that the heat of disgregation and the dielectric constant of a substance are also related phenomena

the latter again varying in an analogous manner with dissociating power, as Nernst has pointed out, and thus we are led back again to a problem which was discussed earlier in this paper—the relationship of dissociation and rotation. As has already been shown, no definite connection can be deduced from the various researches which have been carried out on the subject, but it is nevertheless possible that although the dissociating power of a liquid—a term usually applied to a solvent with regard only to its behaviour towards electrolytes—does not cause actual dissociation in substances other than electrolytes dissolved in that liquid, it may nevertheless modify them. Thus a substance such as ethyl tartrate dissolved in two different liquids may exist in simple molecules in both, but still the force which we call dissociating power is acting to a different extent in each case, and although unable to cause any decomposition of the molecule into ions, may yet exert some other influence on it which will be evident as change of rotation, for instance.

As a summary of the relationships discussed in this paper, the following table may be added. The heat of disgregation is given for 60°, whilst the other figures are for lower temperatures.

The association factors of the solvents have been introduced, as it is of interest to compare their values with the other figures given.

Solvent.	$[\alpha]_D^{20°}$ Infinite dilution	Association factor of solvent.		M.S.V. of ethyl tartrate. Infinite dilution, 20°.	Heat of disgregation of solvent, 60°.	Dielectric constant of solvent.
		Ramsay and Shields.	Traube, 15°.			
Water	+26·2°	1·644* (20°)	2·3†	157·7	523·1	80‡
Methyl alcohol.	11·5	2·32* (20°)	1·79¶	159·3	248·6	32‡
Glycerol	10·6		1·90†	163·3		56·2‖
Ethyl alcohol ..	9·1	1·65* (20°)	1·67†	164	201·6	26·1‡
n-Propyl alcohol	7·4	2·25§ (46·3°)	1·66¶	167·5	175·2	22‡

From this table, and from what has already been said, it appears that a relationship, satisfactory in a qualitative sense, can be

* *Proc. Roy. Soc.*, 1894, **56**, 180.

† These numbers are not quoted by Traube, but are calculated according to his directions.

‡ Nernst, *Theor. Chemie*, 3rd edition, p. 305.

§ Trans., 1893, **63**, 1102.

‖ Thwing, *Zeit. physikal. Chem.*, 1894, **14**, 293.

¶ Traube, Ueber den Raum der Atome, *Ahrens Sammlung*, pp. 32 and 41.

established between variation of rotation in solution and variation of molecular-solution-volume—at least so far as this series of solvents is concerned—and when these phenomena of rotation are traced further back to what may with reason be regarded as the cause of variation of molecular-solution-volume, namely, differences of internal pressure, or what is probably the same thing, of heat of disgregation, very similar regularities are observed, which seems to show that the original assumptions, dependence of volume on internal pressure and rotation on both, are justified.

Finally, it may be pointed out that if the idea developed here be correct, greater account must be taken, when considering the rotation of homogeneous active substances, of their own internal forces; the molecular rotation is not that of a *free* molecule of the compound. The molecular rotation of a homogeneous liquid is the rotation of the molecule subjected to the internal forces of that liquid.

Rotation of ethyl tartrate.

Temperature.	α_D (100 mm.).	Density.	$[\alpha]^t_D$.
10·8°	+8·047°	1·2144	+6·63°
37·6	11·354	1·1873	9·56
33·7	10·842	1·1913	9·10
29·9	10·392	1·1952	8·70
20·1	9·244	1·2051	7·67
100	15·129	1·1230	13·47
89·4	14·725	1·1349	12·97
84·4	14·510	1·1399	12·73
77·1	14·110	1·1472	12·30
67·2	13·600	1·1576	11·75
55·1	12·792	1·1697	10·94
46·1	12·067	1·1789	10·24
25·1	9·900	1·2000	8·25
16	8·719	1·2094	7·21
11·3	8·089	1·2140	6·66

Densities determined:

Temperature.	16·8°	37·2°	46·8°	58·3°	68·1°	76·2°	99·4°
Density	1·2087	1·1878	1·1783	1·1665	1·1566	1·1484	1·1248

Ethyl Tartrate in Water.

The distilled water used in these experiments was well boiled before use.

$p = 1$.

Temperature.	α_D (400 mm.).	Density.	$[\alpha]^{t}_{D}$.
20°	1·043	1·0006	+26·06°
50·8	0·995	0·9945	25·01
27·2	1·026	0·9990	25·67
22·3	1·052	1·0001	26·30

Densities determined:

Temperature	15·8°	26·2°
Density	1·0017	0·9993

$p = 2{\cdot}5$.

Temperature.	α_D (400 mm.).	Density.	$[\alpha]^{t}_{D}$.
14·7°	+2·612°	1·0053	+25·98°
50·3	2·450	0·9940	24·65
27·3	2·572	1·0023	25·66
14·6	2·593	1·0053	25·80

Densities determined:

Temperature.....	14·6°	26·8°	41·6°	55°
Density	1·0053	1·0024	0·9971*	0·9912*

* Although the water used in making up this solution had been boiled, it was found difficult to carry out the density determinations at these higher temperatures owing to the separation of air-bubbles. These two figures are probably therefore too low.

$p = 4{\cdot}999$.

Temperature.	α_D (400 mm.).	Density.	$[\alpha]^{t}_{D}$.
15·3°	+5·304°	1·0110	+26·23°
30·8	5·199	1·0077	25·80
16·6 (after standing 14 days)	5·289	1·0108	26·16

Densities determined:

			After standing 16 days.
Temperature	17·6°	36·1°	14·4°
Density	1·0106	1·0066	1·0113

$p = 9{\cdot}994$.

Temperature.	α_D (400 mm.).	Density.	$[\alpha]^{t}_{D}$.
21·3°	+10·598°	1·0211	+25·95°
14·8	10·701	1·0231	26·17
29·4	10·415	1·0184	25·57
18·6	10·650	1·0220	26·05
20·7 (after standing 5 days)	10·490	1·0213	25·69

Densities determined:

						After standing 5 days.
Temperature.....	19·2°	13°	27·5°	34·4°	14·1°	18·5°
Density.....	1·0220	1·0237	1·0192	1·0164	1·0235	1·0220

$p = 24{\cdot}954$.

Temperature.	α_D (249·6 mm.).	Density.	$[\alpha]^{t}_{D}$.
15°	+15·725°	1·0597	+23·83°
32·5	14·867	1·0511	22·71
25	15·314	1·0549	23·31
20·6	15·505	1·0571	23 55
15	15·747	1·0597	23·85
44·9	14·249	1·0457	21·88
15	15·714	1·0597	23·81

Densities determined:

				After heating to 33·3°.	After heating to 44·9°.
Temperature	16°	23°	33·3°	15·8°	15·2°
Density	1·0594	1·0562	1·0509	1·0595	1·0598

$p = 49{\cdot}993$.

Temperature.	a_D (100 mm.).	Density.	$[a]^{t}_{D}$.
14·7°	+9·759°	1·1193	+17·44°
34·2	9·379	1·1052	16·97
26·8	9·529	1·1102	17·17
19·9	9·670	1·1153	17·34
15·1	9·742	1·1190	17.41
46	9·197	1·0973	16·76
15	9·727	1·1190	17·39
Twelve hours later:			
15·3	9·739	1·1188	17·41
52·6	9·112	1·0927	16·68
14·5	9·750	1·1194	17·42
66·2	8·894	1·0835	16·42
56·1	9·065	1·0903	16·63
15·9	9·704	1·1184	17·35
17	9·689	1·1175	17·34

Densities determined:

						After experiment.
Temperature..	15·7°	22·3°	35·3°	63·8°	70·3°	16·8°
Density	1·1186	1·1137	1·1046	1·0807	1·0752	1·1180

$p = 74{\cdot}99$.

Temperature.	a_D (100 mm.).	Density.	$[a]^{t}_{D}$.
16·2°	+10·069°	1·1707	+11·47°
49·1	11·100	1·1408	12·97
45·0	11·000	1·1446	12·82
30·6	10·587	1·1579	12·19
19·5	10·210	1·1679	11·66
16	10·049	1·1709	11·44
67·2	11·497	1·1248	13·63
53·4	11·194	1·1369	13·13
18	10·144	1·1691	11·57

Densities determined:

					After experiment.
Temperature.....	18·3°	29·7°	41·2°	58°	18·2°
Density	1·1690	1·1588	1·1482	1·1323	1·1691

Ethyl Tartrate in Methyl Alcohol.

The methyl alcohol used was Kahlbaum's best quality and was redistilled from some sodium which had been carefully freed from petroleum.

The density of the methyl alcohol was determined at various temperatures, the following numbers being obtained:

Temperature..	16°	29°	38·4°	48°
Density	0·7953	0·7830	0·7741	0·7646

From these figures, by extrapolation, we find that the density at 0° is 0·8105, whilst, according to Dittmar and Fawsit, the density of pure methyl alcohol at 0° is 0·81015.

$p = 5$.

Temperature.	a_D (400 mm.).	Density.	$[\alpha]^c_D$.
14·8°	+1·845°	0·8120	+11·36°
13·2	1·773	0·8137	10·92
49·2	2·121	0·7796	13·60
40·2	2·081	0·7860	13·24
32·5	1·993	0·7949	12·54
24·3	1·913	0·8029	11·91
12·2	1·750	0·8147	10·74

Densities determined:

				After experiment.
Temperature.....	20·2°	33·8°	46·7°	18·3°
Density	0·8068	0·7939	0·7815	0·8068

$p = 10$.

Temperature.	a_D (400 mm.).	Density.	$[\alpha]^c_D$.
18·9°	+3·744°	0·8240	+11·36°
12·8	3·545	0·8300	10·68
16·7	3·715	0·8288	11·21
53	4·368	0·7905	13·81
46·7	4·320	0·7970	13·55
42·6	4·238	0·8010	13·23
35·5	4·138	0·8080	12·81
27	3·946	0·8162	12·09
16·2	3·695	0·8268	11·17
13	3·615	0·8306	10·88

Densities determined:

					After experiment.
Temperature.....	22°	30·6°	39·6°	45·8°	14·2°
Density	0·8210	0·8128	0·8040	0·7980	0·8286

$p = 25{\cdot}01$.

Temperature.	α_D (249·6 mm.).	Density.	$[\alpha]^t_D$.
18·3°	+6·044°	0·8757	+11·06°
20	6·110	0·8741	11·20
13·2	5·810	0·8807	10·57
48·1	7·068	0·8468	13·37
45·6	6·997	0·8492	13·20
42·8	6·913	0·8518	13·00
39·4	6·813	0·8553	12·76
33·4	6·627	0·8610	12·33
25	6·328	0·8693	11·66
19·2	6·074	0·8750	11·12
18·9	6·065	0·8751	11·10

Densities determined :

Temperature.....	14·1°	27·3°	36°	43·2°
Density	0·8799	0·8671	0·8585	0·8515

$p = 50{\cdot}00$.

Temperature.	α_D (100 mm.).	Density.	$[\alpha]^t_D$.
13°	+4·781°	0·9762	+9·80°
16	4·891	0·9743	10·04
53·8	6·088	0·9366	13·00
46·9	5·968	0·9435	12·65
43·2	5·863	0·9471	12·38
38·2	5·711	0·9521	12·00
34·8	5·616	0·9555	11·76
24·9	5·281	0·9655	10·94
17	4·966	0·9733	10·21
13·2	4·820	0·9770	9·87
14·7	4·908	0·9755	10·06

Densities determined :

Temperature.....	19·8°	34·4°	44·6°	51°
Density	0·9707	0·9561	0·9460	0·9395

$p = 75$.

Temperature.	α_D (100 mm.).	Density.	$[\alpha]^t_D$.
14·9°	+7·012°	1·0879	+8·59°
12·5	6·839	1·0901	8·24
51·1	9·380	1·0504	11·91
45·6	9·014	1·0564	11·38
40·8	8·792	1·0610	11·05
33·7	8·374	1·0685	10·43
24·7	7·767	1·0778	9·61
17·1	7·207	1·0853	8·85

Densities determined:

					After experiment.
Temperature.....	18·3°	32·8°	39·7°	53·2°	17·6°
Density	1·0842	1·0692	1·0626	1·0488	1·0853

Ethyl Tartrate in Ethyl Alcohol.

The ethyl alcohol used was carefully distilled over sodium. Its density was determined with the following results:

Temperature	17·6°	30·4°	41·6°	58·2°
Density	0·7932	0·7822	0·7723	0·7575

This gives, by extrapolation, the number 0·8090 at 0°, whilst Mendeléef found 0·80625 (Landolt-Börnstein).

$p = 5{\cdot}0013$.

Temperature.	α_D (400 mm.).	Density.	$[\alpha]^t_D$.
18·8°	+1·419°	0·8072	+8·79°
17	1·370	0·8090	8·47
11	1·262	0·8143	7·75
13·7	1·304	0·8119	8·03
15·9	1·350	0·8099	8·33
51·8	1·840	0·7779	11·81
42·9	1·729	0·7858	11·01
37·2	1·660	0·7908	10·49
31·1	1·565	0·7961	9·83
21·7	1·417	0·8046	8·80
30·3	1·551	0·7970	9·73
23	1·459	0·8035	9·08

Densities determined:

					After experiment.
Temperature	20·5°	30·6°	38°	54·4°	16°
Density	0·8056	0·7969	0·7900	0·7754	0·8097

$p = 10{\cdot}94$.

Temperature.	α_D (400 mm.).	Density.	$[\alpha]^t_D$.
18·6°	+3·023°	0·8251	+8·37°
7·1	2·553	0·8353	6·98
59·1	4·220	0·7893	12·22
52·8	4·067	0·7950	11·69
41	3·772	0·8052	10·71
23·6	3·243	0·8208	9·03
6·6	2·542	0·8359	6·95

Densities determined:

					After experiment.
Temperature	17·4°	38·4°	55·8°	65·8°	20·2°
Density.....	0·8263	0·8079	0·7922	0·7826	0·8240

$p = 20{\cdot}003$.

Temperature.	α_D (249·6 mm.).	Density.	$[\alpha]^t_D$.
16·2°	+3·348°	0·8569	+7·82°
8·7	2·965	0·8639	6·87
64·4	5·078	0·8119	12·53
59·7	4·945	0·8161	12·14
54	4·803	0·8215	11·71
45·6	4·551	0·8293	10·99
37·9	4·296	0·8367	10·28
23·6	3·756	0·8499	8·85
9·5	3·076	0·8632	7·14

Densities determined:

								After experiment.
Temperature	13·1°	18·9°	33°	35·2°	39°	46·4°	69°	15·6°
Density	0·8595	0·8544	0·8418	0·8397	0·8362	0·8294	0·8074	0·8577

$p = 40{\cdot}002$.

Temperature.	α_D (249·6 mm.).	Density.	$[\alpha]^{t}_{D}$.
19·7°	+7·260°	0·9244	+7·87°
10·2	6·263	0·9334	6·72
60·3	10·335	0·8857	11·69
55	10·058	0·8907	11·31
51·2	9·831	0·8944	11·01
44·9	9·368	0·9004	10·42
40·1	9·063	0·9050	10·03
36·7	8·788	0·9083	9·69
25	7·785	0·9194	8·48
12·4	6·528	0·9312	7·02

Densities determined:

					After experiment.
Temperature.....	16·7°	33·3°	43·8°	62·8°	19°
Density	0·9272	0·9114	0·9017	0·8833	0·9258

$p = 60{\cdot}01$.

Temperature.	α_D (100 mm.).	Density.	$[\alpha]^{t}_{D}$.
21·3°	+4·667°	1·0040	+7·75°
11·1	3·987	1·0141	6·55
14	4·140	1·0113	6·82
56·7	6·480	0·9690	11·24
48·2	6·122	0·9774	10·44
39	5·662	0·9865	9·56
34	5·389	0·9914	9·06
22	4·732	1·0030	7·86

Densities determined:

Temperature	17·5°	28·9°	47·8°	59·1°
Density	1·0079	0·9969	0·9780	0·9668

Ethyl Tartrate in n-*Propyl Alcohol.*

The *n*-propyl alcohol used was of Kahlbaum's best quality and was carefully distilled over clean sodium before use.

Its density was determined at various temperatures with the following results:

Temperature	20°	23·4°	32°	40°	62·8°	69·6°
Density.....	0·8039	0·8012	0·7942	0·7875	0·7682	0·7622

Landolt-Börnstein's tables give d 0°/0° 0·8205 hence d 0°/4° 0·8204, whilst by extrapolation from the above figures we find d 0°/4° 0·8210, so that, judged by the density, the alcohol used seemed almost pure. However, after three solutions had been examined some doubt arose as to whether a portion of one of them had not been returned by mistake to the bottle containing the pure propyl alcohol instead of to that for residues, and to determine this, some of the former liquid was examined polarimetrically and found to have a slight lævorotation. This might be due to presence of ethyl tartrate (although in that case a positive rotation was to be expected), so the propyl alcohol was redistilled and, on examination, the distillate and the residue left in the flask were found to be lævorotatory to almost exactly the same extent, which although proving that no mistake had been made in the first instance, also showed the propyl alcohol to be somewhat impure. This rotation of the alcohol being only very slight and several experiments having already been carried out, it seemed unnecessary to repeat them, since the quantity of impurity present probably did not influence the effect of the propyl alcohol on the rotation of the ethyl tartrate, except by superposition. The rotation of the propyl alcohol was therefore carefully determined:

α_D −0·067° at 18·8° in a 400 mm. tube.
α_D −0·094° at 68·5° „ „

Its rotation is thus very small, but becomes of some importance in the case of dilute solutions, and consequently the results of the experiments performed have been approximately corrected for the rotation of the propyl alcohol, the length of the tube and the composition of the solution examined being taken into account.

$p = 2·5004$.

Temperature.	Obs. α_D (400 mm.)	Corr.	True α_D (400 mm.).	Density.	$[\alpha]^{t°}_D$.
16·1°	+0·488°	+0·066°	+0·554°	0·8152	+6·79°
29	0·614	0·070	0·690	0·8045	8·58
19·4	0·506	0·068	0·574	0·8120	7·07

Densities determined:

Temperature	16·6°	20·9°	32·5°
Density.....	0·8146	0·8111	0·8017

$p = 4{\cdot}9996$.

Temperature.	Obs. α_D (400 mm.).	Corr.	True α_D (400 mm.).	Density.	$[\alpha]^{t}_{D}$.
17·6°	+1·072°	+0·064°	+1·136°	0·8201	+6·93°
20	1·125	0·066	1·191	0·8174	7·29
68·8	1·867	0·091	1·958	0·7763	12·61
62·3	1·775	0·088	1·863	0·7821	11·91
52·6	1·662	0·082	1·744	0·7907	11·03
45·7	1·572	0·079	1·651	0·7970	10·36
28·3	1·308	0·069	1·377	0·8112	8·49
18·4	1·108	0·065	1·173	0·8197	7·16

Densities determined:

						After experiment.
Temperature	16·7°	33·2°	44·9°	58°	80·2°	18·8°
Density	0·8210	0·8075	0·7977	0·7863	0·7661	0·8193

$p = 7{\cdot}713$.

Temperature.	Obs. α_D (400 mm.).	Corr.	True α_D. (400 mm.).	Density.	$[\alpha]^{t}_{D}$.
18·7°	+1·766°	+0·062°	+1·828°	0·8279	+7·16°
55·1	2·751	0·089	2·840	0·7970	11·55
48·7	2·616	0·084	2·700	0·8023	10·90
39·5	2·396	0·077	2·473	0·8102	9·89
28·9	2·082	0·070	2·152	0·8191	8·52
21·3	1·858	0·064	1·922	0·8254	7·55
18·5	1·761	0·062	1·823	0·8279	7·13
13	1·570	0·058	1·628	0·8825	6·34

Densities determined:

						After experiment.
Temperature	23·5°	34·2°	45·8°	58·4°	79·6°	20·8°
Density	0·8236	0·8148	0·8050	0·7941	0·7763	0·8268

$p = 17{\cdot}507$.

Temperature.	Obs. α_D (249·6 mm.).	Corr.	True α_D (249·6 mm.).	Density.	$[\alpha]^{t}_{D}$.
15·9°	+2·354°	+0·035°	+2·389°	0·8596	+6·36°
29·7	3·010	0·040	3·050	0·8480	8·23
19·7	2·555	0 037	2·592	0·8563	6·93

Densities determined:

Temperature.....	18·9°	28·2°
Density.....	0·8570	0·8492

$p = 25$.

Temperature.	Obs. α_D (249·6 mm.).	Corr.	True α_D (249·6 mm.).	Density.	$[\alpha]^{t}_{D}$.
18·9°	+3·626°	+0·033°	+3·659°	0·8799	+6·67°
68·2	6·125	0·053	6·178	0·8358	11·84
63·3	5·945	0·051	5·996	0·8402	11·44
57·9	5·756	0·049	5·805	0·8453	11·01
51·9	5·486	0·047	5·533	0·8509	10·42
42·3	5·076	0·043	5·119	0·8596	9·54
33·1	4·496	0·039	4·535	0·8678	8.37
18·8	3·608	0·033	3·641	0·8800	6·63

Densities determined:

					After experiment.
Temperature	17·7°	31·6°	52·1°	70·6°	19°
Density	0·8810	0·8691	0·8506	0·8334	0·8802

$p = 37{\cdot}51$.

Temperature.	Obs. α_D (100 mm.).	Corr.	True α_D (100 mm.).	Density.	$[\alpha]^{t}_{D}$.
15·9°	+2·082°	+0·011°	+2·093°	0·9259	+6·03°
36	2·939	0·014	2·953	0·9080	8·67
31	2·705	0·013	2·718	0·9122	7·94
23·2	2·395	0·012	2·407	0·9194	6·98

Densities determined:

Temperature	17·8°	35·6°
Density	0·9242	0·9082

$p = 49{\cdot}834$.

Temperature.	Obs. α_D (100 mm.).	Corr.	True α_D (100 mm.).	Density.	$[\alpha]^{t°}_D$.
19°	+3·046°	+0·009°	+3·055°	0·9687	+6·33°
71·2	5·305	0·016	5·321	0·9237	11·56
63·6	5·021	0·015	5·036	0·9262	10·91
58·2	4·830	0·014	4·844	0·9314	10·43
52·4	4·613	0·014	4·627	0·9370	9·91
41·2	4·150	0·012	4·162	0·9479	8·81
28	3·525	0·011	3·536	0·9601	7·39
19	3·031	0·009	3·040	0·9687	6·30

Densities determined:

						After experiment.
Temperature	19·8°	31·2°	43·8°	59·4°	80·2°	18·6°
Density	0·9678	0·9571	0·9453	0·9303	0·9099	0·9696

$p = 74{\cdot}99$.

No correction has been made in this case for the rotation of the propyl alcohol.

Temperature.	α_D (100 mm.).	Density.	$[\alpha]^{t°}_D$.
20°	+5·276°	1·0756	+6·54°
79	9·065	1·0169	11·89
73·6	8·928	1·0221	11·65
69·9	8·791	1·0259	11·43
60·5	8·356	1·0350	10·77
33·8	6·495	1·0622	8·15
47·1	7·605	1·0487	9·67
17·7	5·133	1·0780	6·35

Densities determined:

					After experiment.*	After experiment.*
Temperature	21°	38·3°	50·6°	71·2°	18°	20·8°
Density	1·0747	1·0576	1·0448	1·0248	1·0833	1·0811

* In this case, the density after experiment differs more than is usual from the original density.

Ethyl Tartrate in Glycerol.

The glycerol used was carefully redistilled in a vacuum. It boiled between 177° and 178° under 20 mm. pressure, the temperature of the bath being 225—235°.

Its density was determined at different temperatures with the following results:

Temperature	13·2	30°	54°	75·5°	99·5°
Density.....	1·2651	1·2552	1·2397	1·2256	1·2097

$p = 4{\cdot}985$.

Temperature.	α_D (249·6 mm).	Density.	$[\alpha]^t_D$.
98·2°	+2·12°	1·2080	+14·13°
17	1·52	1·2617	9·68
77·5	1·95	1·2198	12·88
47·6	1·87	1·2425	12·10
35·7	1·77	1·2500	11·38
26·8	1·66	1·2555	10·63

Densities determined:

Temperature	17·1°	40°	57°	99°
Density.....	1·2620	1·2475	1·2366	1·2076

$p = 9{\cdot}906$.

Temperature.	α_D (200 mm).	Density.	$[\alpha]^t_D$.
99°	+3·11	1·2050	+13·01°
17	2·26	1·2600	9·07
78	3·04	1·2193	12·59
72·6	3·00	1·2230	12·28
65·8	2·94	1·2277	12·09
57	2·86	1·2340	11·70
52·7	2·80	1·2365	11·43
17·2	2·25	1·2601	9·01
12·1	2·14	1·2632	8·55

Densities determined:

Temperature.....	17·3	37°	57°	68·2°	99·5°
Density	1·2601	1·2474	1·2338	1·2263	1·2044

$p = 23{\cdot}455$.

Temperature.	α_D (200 mm.).	Density.	$[\alpha]^t_D$.
15·4°	+4·21°	1·2098	+7·42°
100	6·94	1·1944	12·39
75	6·60	1·2125	11·61
68·8	6·44	1·2173	11·28
64·9	6·35	1·2200	11·10
55	5·99	1·2271	10·41
28·3	5·00	1·2460	8·55
25·8	4·87	1·2480	8·32
13	4·18	1·2566	7·09
10·5	4·03	1·2580	6·83
8	3·89	1·2597	6·58

Densities determined:

Temperature	8·5°	21·4°	45·2°	60°	100°
Density	1·2600	1·2512	1·2344	1·2238	1·1944

$p = 48{\cdot}125$.

Temperature.	α_D (200 mm.).	Density.	$[\alpha]^t_D$.
100°	+12·97°	1·1749	+11·47
79	12·14	1·1920	10·58
70·5	11·57	1·1990	10·03
65·8	11·31	1·2030	9·77
51·2	10·49	1·2145	8·98
46·5	9·60	1·2187	8·18
41·8	9·12	1·2222	7·76
39·1	8·89	1·2243	7·54
24	7·24	1·2368	6·08
6·5	4·92	1·2507	4·09

Densities determined:

Temperature	10°	36·3°	55°	70°	100°
Density	1·2480	1·2269	1·2116	1·1993	1·1749

$p = 69{\cdot}93$.

Temperature.	α_D (200 mm.).	Density.	$[\alpha]^t_D$.
98·5°	+18·82°	1·1592	+11·61°
16	7·91	1·2310	4·59
78·4	17·48	1·1763	10·63
70·7	16·62	1·1832	10·03
60·8	15·37	1·1920	9·22
48·5	14·17	1·2028	8·42
40·6	13·04	1·2097	7·71
33·9	11·87	1·2153	6·98
19	8·78	1·2287	5·11

Densities determined:

Temperature	19°	45°	59·5°	80°	97°	100°
Density	1·2289	1·2059	1·1932	1·1752	1·1592	1·1575

$p = 89{\cdot}98$.

Temperature.	α_D (200 mm.).	Density.	$[\alpha]^t_D$.
98·5°	+25·64°	1·1392	+12·50°
15·7	11·72	1·2190	5·34
83	24·49	1·1540	11·79
77·8	24·03	1·1589	11·52
70·2	23·01	1·1665	10·95
66·1	22·41	1·1702	10·64
62·5	21·83	1·1736	10·34
49·5	20·17	1·1865	9·44
37·9	17·77	1·1975	8·25
32·2	16·73	1·2030	7·73
13	11·25	1·2212	5·12

Densities determined:

Temperature	8°	17°	35°	53°	72°	78°	100
Density	1·2271	1·2178	1·2004	1·1828	1·1643	1·1582	1·1377

Experiment with Rochelle Salt, $C_4H_4O_6NaK,4H_2O$.

$p = 13{\cdot}686$.

Temperature.	α_D (400 mm.).	Density.	$[\alpha]^{t°}_D$.
15·6°	+12·737°	1·0711	+21·72°
58·9	12·834	1·0521	22·28
34	12·905	1·0640	22·15
14·8	12·772	1·0715	21·77
99·2	12·482	1·0273	22·34
14	12·760	1·0719	21·74

Densities determined:

Temperature.	15·6°	30·8°	55°	70·1°	14·7°	98·8°
Density	1·0710	1·0654	1·0541	1·0457	1·0714	1·0269

Molecular-solution-volume of Ethyl Tartrate in various Solvents.

$M = 206$. *Molecular volume of ethyl tartrate* at 20° = 206/1·2053 = 170·91
$[\alpha]^{20°}_D = +7{\cdot}67$.

t.	*p.*	*d.*	δ.	M.S.V.	$[\alpha]^{t°}_D$.
Water:					
20°	2·5	1·0041	0·9983	158·25	+25·82°*
,,	5	1·0100	,,	159·06	26·10
,,	10	1·0216	,,	159·44	26·00
,,	24·954	1·0574	,,	160·05	23·60
,,	49·993	1·1153	,,	163·05	17·33
,,	74·99	1·1673	,,	166·50	11·70
10	10	1·0245	0·9997	156·15	26·30
Methyl alcohol:					
20°	5	0·8070	0·7914	159·43	11·50
,,	10	0·8229	,,	160·68	11·48
,,	25	0·8741	,,	161·88	11·20
,,	50	0·9703	,,	164·31	10·50
,,	75	1·0824	,,	166·97	9·12
10	10	0·8327	0·8010	159·24	10·60

* This value is probably rather low.

Molecular-solution-volume of Ethyl Tartrate, &c. (continued).

t.	p.	d.	δ.	M.S.V.	$[\alpha]^{t}_{D}$.
Ethyl alcohol:					
20°	5	0·8061	0·7912	163·57	8·82
,,	10·94	0·8240	,,	165·89	8·57
,,	20	0·8532	,,	165·93	8·30
,,	40	0·9240	,,	166·80	7·90
,,	60·01	1·0054	,,	167·90	7·55
10	10·94	0·8328	0·8000	164·74	7·60
n-Propyl alcohol:					
20°	2·5	0·8113*	0·8043	167·30	7·30
,,	5	0·8183	,,	168·10	7·30
,,	7·713	0·8261*	,,	168·27	7·38
,,	10	0·8339	0·8055†	168·51	6·97
,,	17·507	0·8561	0·8043	167·80	7·00
,,	25	0·8790	,,	169·01	6·73
,,	37·51	0·7222	,,	168·76	6·59
,,	49·834	0·9677	,,	169·56	6·41
,,	74·99	1·0757	,,	169·95	6·54
10	5	0·8267	0·8127	167·27	5·80
Glycerol:					
20°	4·98	1·2600	1·2608	165·44	9·97
,,	9·906	1·2581	,,	166·99	9·30
,,	23·45	1·2521	,,	168·84	7·80
,,	48·125	1·2399	,,	169·17	5·62
,,	69·93	1·2277	,,	169·84	5·19
,,	89·98	1·2149	,,	170·24	6·05
10	9·906	1·2649	1·2665	164·91	8·28
15	9·906	1·2614	1·2638	166·33	8·82

* These are not expetimental values. They have been obtained by interpolation from a density-concentration curve constructed from the other figures. This is rendered necessary by the fact that in so dilute a solution as one of $p=2·5$ a very slight error in density makes a very large error in M.S.V. The experimental values are, for $p=2·5$, $d=0·8118$, and $p=7·713$, $d=0·8265$.

† This experiment was done much later than the others, and when the alcohol used had probably absorbed some moisture.

This research is at present being extended in order that the effect of a considerable number of other solvents, not only upon the rotation of ethyl tartrate, but upon those of other active substances as well,

may be ascertained, and in order to determine whether the ideas suggested here can be further developed so as to explain existing difficulties and discover new regularities.

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XIX.—*On the Union of Hydrogen and Chlorine. Parts I to III.*

By J. W. MELLOR.

THIS paper contains the preliminary results of an investigation, suggested by Professor Dixon, on the mode of formation of hydrogen chloride.

So far as I can gather, William Cruickshank,[1] of Woolwich, was the first to observe the gradual combination of hydrogen and chlorine gases. In reference to the action of chlorine on hydrogen, hydrocarbons, and carbon monoxide he said on August 10, 1801:

"If the pure oxigenated muriatic acid, in the form of a gas, be mixed in certain proportions with any of these inflammable gases and introduced into a bottle filled with and inverted over water, *though no immediate action may be at first perceptible*, yet, in twenty-four hours a complete decomposition will be found to have taken place, the products varying according to the nature of the gases employed. . .

"I introduced into a phial with a glass stopper, filled with and inverted over water, one measure of pure hydrogen and afterwards two measures of very pure oxigenated muriatic gas, this nearly filled the bottle; the stopper was then introduced very tight under water, and before the stopper was introduced, a whitish cloud appeared in the mixture yet *very little or no diminution could be observed* . . .; at the end of twenty-four hours when the stopper was withdrawn the whole of the gas instantly disappeared except about one-tenth of a measure, which was found to be azote, and must have been originally contained in the two measures of oxigenated muriatic acid gas. In this case the products were manifestly common muriatic acid and water, for the water in the phial contained common muriatic acid, but did not in the least smell of the oxigenated."

The words I have italicised appear to be the first record of a phenomenon named, later, the period of induction.

On February 27, 1809, Gay Lussac and Thenard announced that an

[1] Cruickshank, *Nicholson's Journ.*, 1801, [i], **5**, 202. Compare Desormes and Clement, *Ann. Chim.*, 1801, **39**, 26; Berthollet's "Essai de Statique Chimique," 1803, **1**, 423.

explosive combination occurs when a mixture of hydrogen and chlorine gases is exposed to direct sunlight.[1] In June of the same year, John Dalton showed the influence of light in this reaction, and on repeating Cruickshank's experiment, also observed that "the gases after being put together (over water) seemed to have no effect for one or two minutes, when suddenly the mixture began to diminish with rapidity."[2]

In a letter to Goethe in 1810, Seebeck intimated that a mixture of hydrogen and chlorine gases contained in a clear glass vessel detonated in the sunshine, whilst under a dark blue glass combination occurred without explosion in one minute, and under a dark red glass the action either took place very slowly or not at all.[3] This observation was more particularly investigated by Berard (1813),[4] Draper (1843),[5] Favre and Silbermann (1853),[6] and finally by Bunsen and Roscoe (1857).[7]

Draper took up the subject about 1840, and made an instrument, called the tithonometer, to measure the rate of combination of hydrogen and chlorine under the influence of light. The action of his instrument is based on the fact that the hydrogen chloride formed is at once absorbed by the liquid in the same vessel. The resulting contraction is measured on a suitable index. Draper believed that the first action was to induce a more active, allotropic modification of chlorine, for he found that insolated chlorine combines with hydrogen more readily, and even in the dark. The period of inertness, previously noted by Cruickshank and Dalton, was then also suppressed. This allotropism was not confirmed by Bunsen and Roscoe (1855), or by Askenasy and Meyer (1892),[8] although Favre and Silbermann (1853), and Amato (1884) have given experimental evidence in favour of Draper's original statement. Fremy and Becquerel believe it to be due to the presence of oxychlorine compounds formed by the action of chlorine on the water vapour present.[9] Draper also records that if an intense light, such as that of a spark from a Leyden jar, be momentarily

[1] Gay Lussac and Thenard, *Mem. phys. Chim. Soc. d'Arcueil*, 1809, **2**, 340, or Gilbert's *Ann.*, 1810, **35**, 8. Alembic Club Reprints, No. 13, p. 43.

[2] Dalton's "A New System of Chemical Philosophy," 1811, **2**, 189.

[3] Seebeck, "Von der Chemischen Action des Lichts und der farbigen Beleuchtung," in Goethe's "Zur Farbenlehre," Tübingen, 1810, quoted in Eder's "Geschichte der Photochemie und Photographie," 1891, **1**, 73.

[4] Berard, *Ann. Chim.*, 1813, **85**, 309.

[5] Draper's "Collected Memoirs," 1878; *Phil. Mag.*, 1843, [iii], **23**, 401; 1845, [iii], **27**, 327.

[6] Favre and Silbermann, *Ann. Chim. Phys.*, 1853, [iii], **37**, 479.

[7] Bunsen and Roscoe, *Pogg. Ann.*, 1855, **96**, 373; 1857, **100**, 43, 481; 1857, **101**, 235; 1859, **108**, 193; 1862, **117**, 529; *Phil. Trans.*, 1857, **146**, 355, 601; 1859 **148**, 879; Ostwald's "Klassiker," Nos. 34 and 38.

[8] Askenasy and V. Meyer, *Annalen*, 1892, **269**, 72.

[9] Becquerel and Fremy, Wurtz's "Dictionnaire de Chimie," 1879, **2**, 255.

flashed on to the mixture, a sudden expansion, followed instantly by a return to the original volume, takes place (therefore no formation of hydrogen chloride). This phenomenon will be named, after its first observer, the "Draper effect."

Favre and Silbermann[1] found that the heat developed in the action of insolated chlorine on potash was greater than that of non-insolated chlorine by some 39 cal. The increase in the activity of the chlorine is not accompanied by a change in volume.

The first part of Bunsen and Roscoe's classical work appeared in 1855. The final result was the establishment of the more important laws of the chemical action of light. These investigators, by means of a perfected form of Draper's tithonometer, found that an amount of actinic energy disappeared in the act of photochemical combination equivalent to the amount of light absorbed. This phenomenon was styled "photochemical extinction." After the period of inertness, observed by Cruickshank, the rate of combination of hydrogen and chlorine was found to gradually increase until a maximum steady state was attained (period of acceleration[2]). The interval between the first impact of light and the period of constancy was termed the period of "photochemical induction." Bunsen and Roscoe also found that the presence of minute traces of oxygen, or of an excess of either of the reacting components, considerably retarded the rate of formation of hydrogen chloride. Gautier and Helier,[3] under somewhat different conditions, found an acceleration in the rate when either of the reacting gases is present in excess. This is what the dynamical theory of mass action would lead us to expect.

In 1871, Budde[4] discovered that when chlorine is exposed to a source of actinic light it occupies a greater volume. This expansion cannot be attributed to the direct effects of heat. Recklinghausen[5] (1894) found that a photo-expansion also occurs when the chlorine is mixed with hydrogen, carbon monoxide, or ethylene. No change in volume occurs when perfectly pure and dry chlorine is exposed to light under somewhat similar conditions (Baker[6] and Shenstone[7]).

Since Bunsen and Roscoe's great work, the most important contribution to the subject was published by Pringsheim[8] in 1887. Prings-

[1] *Loc. cit.*

[2] Veley, *Phil. Mag.*, 1894, [v], **37**, 165.

[3] Gautier and Helier, *Compt. rend.*, 1897, **124**, 1121.

[4] Budde, *Phil. Mag.*, 1871, [v], **42**, 290; *Pogg. Ann. Ergbd.*, 1873, **6**, 477. See also Richardson, *Proc. London Phys. Soc.*, 1891, **11**, 185.

[5] Recklinghausen, *Zeit. physikal. Chem.*, 1894, **14**, 494.

[6] Baker, *Brit. Assoc. Rep.*, 1894.

[7] Shenstone, Trans., 1897, **71**, 471.

[8] Pringsheim, *Wied. Ann.*, 1887, **32**, 384; Dixon and Harker, *Mem. and Proc. Manchester Lit. Phil. Soc.*, 1889, [iv], **3**, 118.

heim rediscovered the Draper effect, and also found that by drying the mixed electrolytic gases the rate of combination was retarded, for in sunlight the reaction was only accompanied by a feeble clicking sound ("ein sehr schwaches knisterndes Geräusch"). Pringsheim believes that during the period of induction some such intermediate compound as chlorine monoxide is formed by the action of chlorine on the water vapour present.

A most interesting observation has just been recorded by Cordier[1] somewhat to the effect that dry chlorine is transparent, but moist chlorine opaque, to the actinic rays.

It has been my purpose to investigate the mode in which light effects the combination of hydrogen with chlorine. With this object in view, I began by studying the electrolysis of hydrochloric acid, and the solution of chlorine in this acid, since an exact knowledge of these processes is necessary to interpret the work of previous investigators.

I.—The Electrolysis of Hydrochloric Acid.

The general and most convenient mode of preparing a mixture of equal volumes of hydrogen and chlorine gases (Chlorknallgas) is by the electrolysis of hydrochloric acid, under the conditions Bunsen and Roscoe[2] found to be most favourable.

I have examined the gases prepared by this method with a view to finding what impurities, if any, are present. The highly successful experiment of Baker[3] in which a dried mixture of hydrogen and chlorine, prepared by another process, did not completely combine when exposed for two days to the direct rays of the sun, has not been equalled by the use of the electrolytic gases.

Bunsen and Roscoe have also shown that the influence of impurities in modifying the rate of combination of electrolytic hydrogen and chlorine is most remarkable. "The amount of foreign gas sufficient to materially disturb the normal rate cannot approach the billionth part of the total volume of the gas."

Draper[4] has stated that the electrolysis of hydrochloric acid never yields equal volumes of hydrogen and chlorine. Bunsen and Roscoe, however, very carefully studied the action, and came to the conclusion that small variations from equality in the proportions of the two gases can be brought within the limits of analysis by taking

[1] Cordier, *Monatsh.*, 1900, **21**, 660.

[2] Bunsen and Roscoe, *Pogg. Ann.*, 1855, **96**, 373.

[3] Baker, Trans., 1894, **65**, 611. It might also be pointed out that 25 per cent. of the mixture remained uncombined after four days exposure, two of which were of bright sunshine.

[4] Draper, *loc. cit.*

suitable precautions and keeping the strength of the acid over 23 per cent. of hydrogen chloride.[1]

If, during the electrolysis of concentrated hydrochloric acid, $4HCl + 2H_2O$ are decomposed to form $2HOCl + Cl_2 + 3H_2$, the electrolytic gases would consist of $(m+n)H_2$ and $(mHOCl + nCl_2)$, neglecting the hydrogen chloride and steam present. If a cylinder containing these gases be opened under an aqueous solution of potassium iodide, then for every four volumes of HOCl present a quantity of iodine equivalent to two volumes of chlorine will be liberated. In Bunsen and Roscoe's analyses there is a mean error of $-0{\cdot}72$ per cent., assuming that the mixture contained equal volumes of the gases. Therefore, unless the electrolytic gases contain as impurity an amount of HOCl vapour exceeding 0·18 per cent., it would have escaped detection.[2] A slight excess of hydrogen would also occur if a very little water were decomposed in the electrolysis.

A large amount of matter has been published on the electrolysis of the hypochlorites and chlorides. The following refers to hydrochloric acid.

Riche[3] (1858) observed that dilute hydrochloric acid yields perchloric acid when a current from 10 Bunsen cells is passed through it.

Tommasi[4] (1882) found chlorine oxides at the positive pole even with concentrated acid, and pointed out the possibility of their formation by the decomposition of the hydrate, $HCl,6H_2O$, or by the action of oxygen or water on the electrolyte.

Haber and Grinberg[5] (1898), in a very complete investigation, confirm Bunsen and Roscoe's observation. Working on small quantities, they have shown that concentrated hydrochloric acid, with platinum electrodes, furnishes a 100 per cent. yield of chlorine, which falls to zero with increasing dilution. They also trace the presence of varying quantities of oxygen, perchloric, chloric, and hypochlorous acids to the combination of Cl ions with the OH ions of water.[6]

The great solubility of the liberated chlorine and its diffusion over to the cathode is, no doubt, an important factor in the inducing of secondary actions.[7] It is this that causes the electrical sign of the

[1] It is interesting to observe in this connection that E. Morley (*Zeit. physikal. Chem.*, 1896, **20**, 430) was unable to obtain an electrolytic mixture of hydrogen and oxygen in the proportions $H_2 : O$ by the electrolysis of water.

[2] Bunsen, *Annalen*, 1853, **86**, 273.

[3] Riche, *Compt. rend.*, 1858, **46**, 350.

[4] Tommasi, *Compt. rend.*, 1882, **95**, 689.

[5] Haber and Grinberg, *Zeit. anorg. Chem.*, 1898, **16**, 198; **18**, 37.

[6] Matteucci found that the more intense the current, the greater the amount of oxygen evolved (Gmelin's "Handbook of Chemistry," Eng. ed., 1848, **1**, 455).

[7] Townsend, *Proc. Camb. Phil. Soc.*, 1897, **11**, 245, or *Phil. Mag.*, 1898, [v], **45**, 25; Enright, *Phil. Mag.*, 1890, [v], **49**, 56.

liberated hydrogen to change from its initial positive value to a final negative one. The formation of oxygen compounds of chlorine by the dissociation of chlorine water was first indicated by Millon [1] in an equation subsequently developed by Jakowkin [2] in the following form :

$$Cl_2Aq \rightleftarrows (HOCl + \overset{+}{H} + \overset{-}{Cl})Aq.$$

The electrolysis of aqueous solutions of chlorine is said to lead to the production of hydrochloric acid at the negative pole, and of chloric acid at the positive pole.[3] Oettel [4] has shown that nascent hydrogen at the cathode recombines with the chlorine in the solution.

Gautier and Helier [5] say, "L'électrolyse de l'acid chlorhydrique ou des chlorures fournissent, à chaud ou à froid, un gaz mêlá d'oxyde de chlore, comme ou peut s'en assurer en le faisant passer, après dessiccation préalable, dans un tube de porcelain chauffé au rouge, en receuillant dans une éprouvette pleine de potasse les gaz dégagés, il reste toujours de l'oxygène rallumant les corps en ignition." On carefully repeating this experiment, my equivalent to their "tube de porcelain chauffé au rouge" was broken by regurgitation of the potash solution. The experiment succeeds equally well without the hot tube.

The following experiments prove that variable quantities of oxygen are evolved during the electrolysis of concentrated hydrochloric acid.

Series 1.—Pure cold hydrochloric acid saturated with dry hydrogen chloride gas was subjected to electrolysis in a cell from which the spent acid could be removed and new acid introduced without admission of air (see Fig. 1, p. 222). The electrode gases were led off separately on account of the subsequent heating of the anode gases, otherwise explosive combination occurs at 430—440°. [6] The prepared carbon electrodes were cemented in while warm with a pulp of asbestos and sodium silicate (water glass). In other respects Bunsen and Roscoe's directions were closely followed.

(a). The anode gases were led through a three-way cock and two Mitscherlich absorption bulbs, the one containing water the other concentrated sulphuric acid of sp. gr. 1·9 ; then over fragments of glass wet with the same acid in a V-tube [7] ; thence through a heated glass tube,

[1] Millon, *Compt. rend.*, 1849, **28**, 42.

[2] Jakowkin, *Ber.*, 1897, **30**, 518 ; E. Muller, *Zeit. Elektrochem.*, 1900, **6**, 573.

[3] Balard, *J. pr. Chem.*, 1835, **4**, 167.

[4] Oettel, *Chem. Centr.*, 1895, [iv], **7**, ii, 3.

[5] Gautier and Helier, *Compt. rend.*, 1897, **124**, 1129, 1267.

[6] Meyer and Freyer, *Ber.*, 1893, **26**, 428.

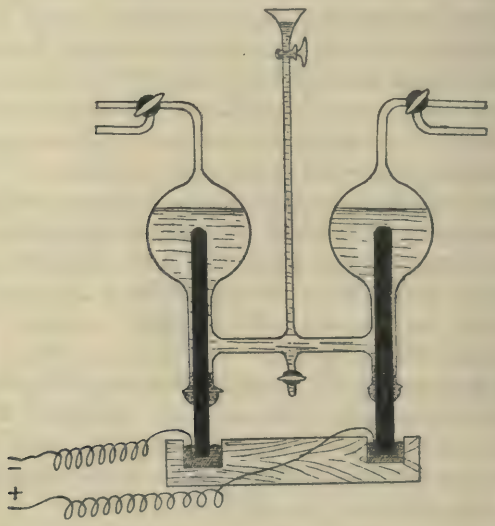
[7] Bailey and Fowler (Trans., 1888, **53**, 755) have shown that if the gas contains traces of hydrogen chloride, the reaction $2P_2O_5 + 3HCl = POCl_3 + 3HPO_3$ occurs. Chromic and copper compounds are objectionable for removing the hydrogen chloride on account of the possible action of hypochlorous acid. Hence it appeared better not to use phosphoric oxide (compare Gutmann, *Annalen*, 1898, **299**, 267 ; Baker,

and finally collected in an eprouvette over an aqueous solution of potassium hydroxide. Air was carefully swept out of the apparatus by means of a current of chlorine, prepared by Gautier and Helier's process, until a blank experiment gave no result. The gases evolved during the first two hours electrolysis escaped *viâ* the three-way cock. The different parts of the apparatus were sealed together before the blowpipe. The experiments were done in a dark cellar.

In an average experiment, approximately 13—14 litres of the anode gases gave 1·2 c.c. of oxygen (at normal temperature and pressure) in successive measurements of 0·4, 0·1, 0·3, and 0·4 c.c.

(b). The dried cathode gases, from which chlorine and hydrogen had

FIG. 1.—*Electrolytic vessel.*



been removed, were passed through a *temoin* tube and then over warm palladium asbestos.[1] The water was absorbed in a weighed phosphoric oxide tube. Air was, as before, swept out of the apparatus by a current of hydrogen previous to an experiment.

No perceptible increase in weight was noticed.

The large quantity of desiccating agents used in these experiments is a serious objection. E. Morley[2] has shown that a slow current of

Trans., 1898, **78**, 422). Calcium chloride cannot be used, for any chlorine monoxide present would form hypochlorites (Garzarolli-Thurnlackh and Schachal, *Annalen*, 1885, **230**, 280).

[1] Winkler's "Anleitung zur chemische Untersuchung der Industrie-Gase," 258, (1877).

[2] Morley, *Amer. J. Sci.*, 1885, [iii], **30**, 140.

air, passed through strong sulphuric acid, failed to remove something like 0·002 milligram of water per litre. This amount of moisture passed along with chlorine through a red hot tube would probably liberate oxygen, but not sufficient to account for that obtained. The absorption of oxychlorine compounds, as well as of hydrogen chloride, would take place in the first washing bulbs. Whatever the method by which Gautier and Helier performed their "dessiccation prélable," their hot tube is unnecessary, for the experiment succeeds equally well without it.

Unfortunately, there is no satisfactory means of detecting hypochlorous acid (or chlorine monoxide) under the conditions of these experiments, as was shown by Haber and Grinberg [1] in a recent examination of the delicacy of the various methods proposed for the detection of hypochlorous acid in the presence of hydrochloric acid. They also point out that Wolter's method,[2] used by Pedler [3] to establish an equation for the action of light on chlorine water, is quite unreliable for "nachweisbare Mengen unterchloriger Säure können selbst in $\frac{1}{1000}$ norm. Salzsäure nicht mehr bestehen." Millon's [4] manganous chloride test can, however, be used as a "Vergleichsprobe" with chlorine water, hypochlorous acid giving a brown colour rapidly, chlorine water slowly. Jakowkin [5] confirms this observation and says, "es est deshalb ganz unerklarlich, auf welche Weise Pedler die Anwesenheit von HClO in einer Chlorlösung, welche (nach der Belichtung) überschüssige Salzsäure enthielt, konstatiert hatte."

Series II.—A double globe (Fig. 2) had at one end three necks—two wider ones for carbon electrodes, and a central one carrying a two-way cock (*a*)—on the other end was sealed a capillary tube, bent twice at right angles, and carrying a three-way cock (*d*). The free end of the capillary had a piece of wider glass tubing sealed on, as shown in the figure, p. 224.

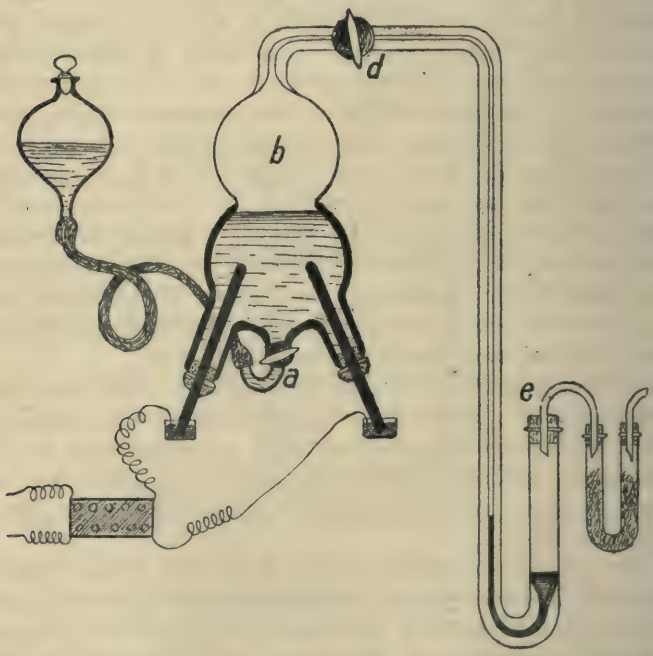
The lower globe was painted black. Both globes were filled with concentrated hydrochloric acid (completely saturated with hydrogen chloride in the cold) as far as the three-way cock, which was lubricated with glacial phosphoric acid. This filling was easily done by dipping the tip of *a* in the acid and connecting *d* with an aspirator, or as shown in the figure. The upper cock *d* was then closed, and the lower one partially so. An electric current was switched on (2—4 volts), and while the globe *b* was being filled with electrolytic gas, the capillary tube, on the side of the apparatus, was filled with concentrated sulphuric acid by pouring the acid in *e* and applying suction at *d*. A drying tube was then fitted on to *e*.

[1] *Loc. cit.* [2] Wolters, *J. pr. Chem.*, 1873, [ii], **7**, 468.
[3] Pedler, Trans., 1890, **57**, 613. [4] *Loc. cit.*
[5] Jakowkin, *Zeit. physikal. Chem.*, 1899, **29**, 613.

When the globe b was almost full of the electrolytic gas, the cock at a was closed, and d opened for some two hours. The right and left hand sides of the vessel were then put into communication, and the upper globe exposed to some source of artificial light (coal gas lamp). The current was so regulated by the introduction of a suitable resistance that the ratio of the rate of formation of the gases $H_2 + Cl_2$ and the rate of solution of the reformed HCl was approximately constant.

After 14 days, the three-way cock d was joined to a Hempel burette containing an aqueous solution of manganous chloride, and the current

FIG. 2.



stopped. All the air between the capillary of the cock and the burette was driven over into the right hand side of the apparatus. Water was then run into the lower cock, until all the gases in the upper globe were transferred to the burette. Analysis, by Haber and Grinberg's method, invariably showed that oxygen is formed during the electrolysis.

From this and the preceding experiments, it follows that if x be the amount of oxygen in the vessel at the end of the time t, we have:

$$x = \phi(t).$$

The manganous chloride comparison test generally shows the presence

of traces of hypochlorous acid, thus confirming the suspicion of Haber and Grinberg.

The gases exposed to the light are, therefore, a mixture of chlorine, hydrogen, steam, hydrogen chloride, and oxygen. There is probably a condensation of water vapour on the glass. A reaction between chlorine and water is, therefore, quite possible. From the thermodynamical principle of maximum work, it can be shown that, while gaseous chlorine will not decompose steam at 100°, it will act slowly on water at atmospheric temperatures. Thus, in round numbers :

(1). *Water Vapour and Chlorine Gas.*

$[H_2,O]$ gas at $100° = +58$ Cal. ; $[H,Cl] = +22$ Cal.

$$H_2O\ (gas) + 2Cl\ (gas) = 2HCl\ (gas) + O\ (gas) - 14\ Cal.$$

(2). *Liquid Water and Chlorine Gas.*

$[H_2,O]$ liquid $= 68{\cdot}4$ Cal. ; $[HCl,Aq] = +17{\cdot}2$ Cal.

$$H_2O\ (liquid) + 2Cl\ (gas) + Aq = 2HClAq + O\ (gas) + 10\ Cal.$$

Under similar conditions, in a cool cellar and an atmosphere of moist chlorine in the globe *b*, a negative result was obtained.[1]

It is thus evident that :

(1). Oxygen is present among the gaseous products of the electrolysis of hydrochloric acid.

(2). Even though traces of the lower chlorine oxides may be formed during the electrolysis, it is unlikely that any escape a preliminary washing of the gases.

II. The Solubility of Chlorine in Aqueous Hydrochloric Acid.

When a mixture of equal volumes of hydrogen and chlorine in the presence of water saturated with the two gases is exposed to the action of light, hydrogen chloride is formed by the water at a rate proportional to the intensity of the light. Thinking that this absorption of the hydrogen chloride might disturb the equilibrium of the gases in the insolation vessel of Bunsen and Roscoe's actinometer, I have investigated the solubility of chlorine in water containing varying quantities of hydrogen chloride at a constant temperature.

[1] See the various reports to the British Association collected by Richardson (*B. A. Reports*, 1888, 89 ; 1889, 59 ; 1890, 263). Bunsen and Roscoe (this Journ., 1856, **8**, 190), investigating Wittwer's proposal (*Pogg. Ann.*, 1855, **94**, 527) to measure the chemical action of light by the decomposition of chlorine water [say, $2Cl_2$ (liquid) + $2H_2O$ (liquid) = $4HCl$ (liquid) + O_2 (gas)], found that the presence of hydrochloric acid greatly retarded the action.

No systematic work appears to have been done on this subject. Three isolated records were all I could find.

In 1856 Roscoe [1] found that the presence of 1/120th part of hydrogen chloride lowered the value of the coefficient of absorption of chlorine in water from $\alpha = 2{\cdot}3911$ to $1{\cdot}9789$ at 14°.

Berthelot [2] (1880) found that a 38 per cent. solution of hydrogen chloride absorbs 17·3 grams of chlorine per litre; a solution containing 1/3HCl, that is, 33 per cent., [3] absorbs 11·0 grams; whilst a 3 per cent. solution absorbs 6 grams of chlorine per litre (temperature not stated). Berthelot suspects the formation of hydrogen perchloride, HCl_3, in strong solutions, and quotes thermochemical data in support of this view.

Goodwin [4] (1882) investigated the influence of temperature on the solubility of the following different strengths of acid and found:

Hydrochloric acid of sp. gr. 1·046, $\alpha = 2{\cdot}5403$ at 23·6° (752 mm.).
" " " 1·080, $\alpha = 4{\cdot}1433$ at 15·5° (763 mm.).
" " " 1·125, $\alpha = 4{\cdot}7631$ at 20·7° (762 mm.).

In my preliminary work I found that Heidenhain and V. Meyer's [5] method for saturating the liquid by shaking with the gas did not work so satisfactorily as the one described below.

Chlorine, evolved from the liquid, was washed in boiled distilled water, then in chromic acid solution, and again in water. The gas was then passed into a vessel containing the given solution until two titrations, with sodium thiosulphate, showed constant figures. The saturation vessel stood in a water-bath maintained at a temperature of 20—21° by means of a thermostat.[6] This work was done in a dark cellar.

Ten c.c. of the saturated solution were run [7] into an aqueous $N/10$ solution of potassium iodide. The free iodine was determined by

[1] Roscoe, this Journ., 1856, **8**, 14.

[2] Berthelot, *Ann. Chim. Phys.*, 1881, [v], **22**, 462; or *Compt. rend.*, 1880, **91**, 194.

[3] A. M. Comey, "Dictionary of Solubilities," 105, 1896, translates this as one-third of the 38 per cent. solution, and, therefore, wrongly reads "12·7 per cent. HCl absorbs 11 grams of chlorine per litre."

[4] Goodwin, *Trans. Roy. Soc. Edin.*, 1882, **30**, 597; or *Ber.*, 1882, **15**, 3039.

[5] Timofeeff, *Zeit. physikal. Chem.*, 1890, **6**, 141.

[6] This temperature was chosen to eliminate, as far as possible, any disturbance due to the formation of hydrates (compare Roozeboom, *Rec. trav. Pays-Bas*, 1884, **3**, 59; 1885, **4**, 69; Isambert, *Compt. rend.*, 1878, **86**, 481).

[7] The slight loss of chlorine involved in the withdrawal of this liquid by a suction pipette is avoided by using a pipette similar to that described by Reid (*Chem. News*, 1892, **66**, 167), or Ruting's patent pipette (*Zeit. physikal. Chem.*, 1899, **29**, 626).

means of standardised sodium thiosulphate solution in the usual way. The loss due to the decomposing effect of hydrochloric acid on the thiosulphate[1] was negligibly small, since the thiosulphate was added direct to the iodine.[2]

Let θ be the temperature, p the height of the barometer in mm. of mercury, α the coefficient of absorption, λ the coefficient of solubility, n the number of c.c. of the standard thiosulphate required in titrating, v the volume of chlorine in c.c. absorbed by the given solution. Since each c.c. of the thiosulphate solution was equivalent to 0·01386 gram of iodine, or 0·003848 gram or 1·2127 c.c. of chlorine, that is, $v = 1·2127$,

$$\alpha = \frac{273}{273+\theta} \cdot \frac{p}{760} \cdot \frac{v}{10}.$$

For chlorine in pure water at 21°, $\alpha = 2·1167$, Schönfeld[3] gives 2·1148. The variations in the barometer readings were so small that their influence on the results is well within the errors of experiment. Temperature variations were, for the same reason, neglected. Hence:

$$\lambda = \alpha \frac{273+\theta}{273} = n \times 1·2127.$$

Absorption coefficients of chlorine.

Grams HCl per 1000 c.c.	n.	p.	$t°$.	Grams Cl_2 per 1000 c.c.	α.	λ.
313·401	31·52	761	21·0	12·03	3·5492	3·8224
282·060	29·57	761	21·0	11·37	3·3278	3·5859
250·720	27·77	759	21·0	10·68	3·1272	3·3677
219·380	25·82	759	21·0	9·93	2·9243	3·1312
188·040	24·01	761	20·2	9·23	2·7020	2·9117
156·700	22·30	761	20·2	8·58	2·5095	2·7043
125·360	20·18	761	20·5	7·76	2·2711	2·4473
94·020	18·70	760	20·5	7·19	2·1044	2·2677
62·680	16·60	760	20·0	6·38	1·8682	2·0131
31·340	14·87	762	21·0	5·81	1·6736	1·8033
15·670	13·27	759	21·0	5·10	1·4933	1·6092
12·540	12·61	759	21·0	4·85	1·4200	1·5292
9·402	12·38	760	21·0	4·76	1·3942	1·5013
6·248	12·87	760	20·0	4·94	1·4483	1·5607
3·134	13·77	760	21·0	5·30	1·5496	1·6698
nil	18·80	760	21·0	7·23	2·1157	2·2799

When the amounts of hydrogen chloride contained in the solution are plotted as abscissæ against the amounts of chlorine absorbed, two

[1] Pickering, this Journ., 1870, **37**, 135.
[2] Norton, *Amer. J. Sci.*, 1899, [vii], **7**, 237.
[3] Schönfeld, *Annalen*, 1855, **93**, 26.

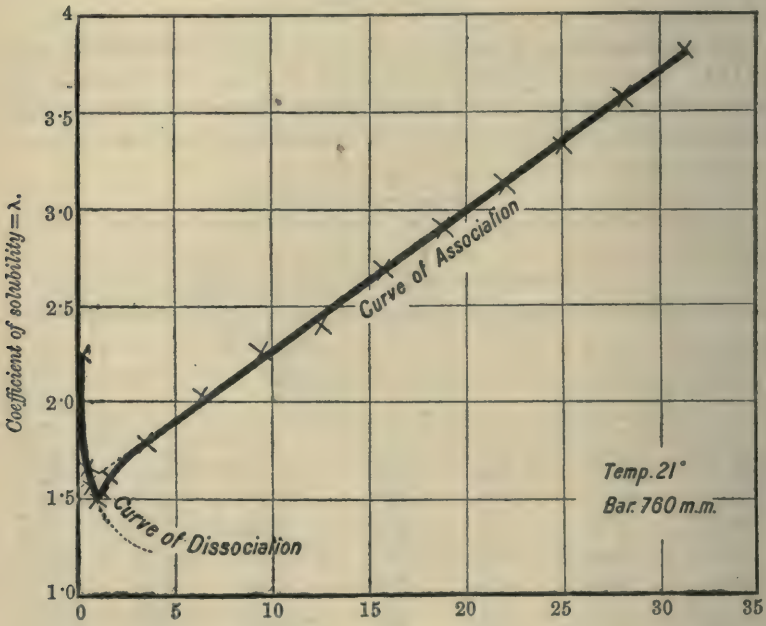
distinct curves appear. The one is subsequently referred to as the "curve of dissociation," the other as the "curve of association."

The first action of chlorine on dilute hydrochloric acid is apparently represented by some exponential curve which intersects another simpler linear curve represented by the equation:

$$\beta = ap + b$$

where a and b are constants approximately equal to 0·023 and 4·92 respectively, and p and β respectively denote the amounts of hydrogen chloride and of chlorine per 1000 c.c. of solution.

FIG. 3.



Isothermal curve of the solubility of chlorine in aqueous solutions of hydrochloric acid of varying concentration.

Jakowkin[1] has proved that the action of chlorine on water is a reversible dissociation somewhat in the form of the equation:

$$Cl_2Aq \rightleftarrows (HCl + HOCl)Aq.$$

He takes advantage of the fact that undissociated chlorine divides in a known ratio between water and carbon tetrachloride, in order to

[1] Jakowkin, *Zeit. physikal. Chem.*, 1899, **29**, 613.

determine the amounts of dissociated and undissociated chlorine in aqueous solution, hydrochloric and hypochlorous acids being insoluble in carbon tetrachloride.

According to the dissociation theory, $HClAq \rightleftarrows (\overset{+}{H} + \overset{-}{Cl})Aq$, while the hypochlorous acid suffers little if any dissociation. The latter statement is confirmed by (1) its weak acidity; (2) its easy hydrolysis with strong bases; (3) the rapid increase of its molecular conductivity with dilution; and (4) its normal molecular weight by cryoscopic methods.

Even in darkness the action is termolecular,

$$Cl_2Aq \rightleftarrows (\overset{+}{H} + \overset{-}{Cl} + HOCl)Aq,$$

and is therefore denoted by the formula

$$K = \frac{(A-c)^3}{c} \quad . \quad . \quad . \quad . \quad (1)$$

where A represents the total number of gram-molecules of chlorine in the solution, c that of the undissociated chlorine, $A-c$ the number of dissociated chlorine molecules in the solution.

The total volume of a substance taken up by unit volume of solvent is often referred to as the *apparent solubility*, whilst the amount of substance which remains unchanged in unit volume of solution is termed the *real solubility*.

Applying Nernst's distribution law,[1]

$$A = c + (A-c),$$

and since for every $\overset{+}{Cl}$ ion that goes to form HOCl one $\overset{+}{H}$ ion is set free, we have, according to the mass law,

$$cK = (A-c)^2 \quad . \quad . \quad (2)$$

where K has not necessarily its former value.

If c_2 is the concentration of a second electrolyte which has one ion in common with the ions already in solution, we have for H or Cl ions, as before,

$$A' = c' + (A'-c'),$$

and

$$c'K' = (A'-c')(A'-c'+c_2) \quad . \quad . \quad (3)$$

But since

$$(A-c) < (A'-c')$$
$$c' > c,$$

that is, the amount of undissociated chlorine will be increased by the addition of a second electrolyte containing either H or Cl ions; hence

[1] Nernst, *Zeit. physikal. Chem.*, 1889, **4**, 372; Noyes, *ibid.*, 1890, **6**, 241.

it follows from the "theorem of constant solubility" that the solubility of chlorine will be diminished.

Let λ represent the apparent solubility, and χ the real solubility of chlorine in hydrochloric acid, x the amount of chlorine or of dissociated $(\overset{+}{H}+\overset{-}{Cl})$ in solution according to Jakowkin's equation, y the amount of chlorine in solution assumed, for the present, to be in some way combined with HCl. Hence

$$\lambda = \chi + x + y.$$

For dilute solutions we should have

$$\lambda = \chi + x.$$

The value of x is easily calculated from the dissociation data compiled by Fitzgerald in the Reports to the British Association, 1893.[1] The results are not altogether in accord with experiment, showing that under these conditions χ is either not constant, or y cannot be neglected. Beyond a certain limit, however, y becomes relatively large, while x becomes small. That is

$$d\lambda = \frac{\partial x}{\partial y}dy + \frac{\partial y}{\partial x}dx.$$

assuming χ to be constant.

This diminution in the solubility of chlorine can be readily shown in a qualitative way, by adding a few c.c. of concentrated hydrochloric acid to a quantity of saturated chlorine water contained in a narrow vessel. Bubbles of chlorine soon form and escape to the surface.

It is evident from the termolecular action of chlorine on water:

(1) The addition of an electrolyte capable of supplying Cl ions to the solution will cause a diminution in the solubility of chlorine.

Thus Kumpf,[2] Goodwin,[3] and Jakowkin[3] have shown this diminution in the solubility of chlorine in saturated solutions of alkali chlorides. The separation of sodium chloride, when chlorine is passed into saturated aqueous solutions, is another consequence of the same law. Conversely, Engel has shown[4] that the addition of hydrogen chloride diminishes the solubility of electrolytic chlorides. Non-electrolytic chlorides, however, do not influence the solution unless molecular association occurs: for example, mercuric chloride.

(2) The addition of an electrolyte capable of supplying H ions must also effect a reduction in the solubility of the chlorine.

This has been proved, for the electrolytic acids, nitric acid, hydro-

[1] Reprinted in Whetham's "Solution and Electrolysis," 215, (1895).

[2] Kumpf (*Inaug. Dissert.*) *Wied. Biebl.*, 1882, **6**, 276.

[3] *Loc. cit.*

[4] Engel, *Bull. Soc. Chim.*, 1889, [iii], **1**, 695; or *Compt. rend.*, 1889, **104**, 1710; Ditte, *Ann. Chim. Phys.*, 1897, [vii], **10**, 556.

chloric acid, sulphuric acid, and acetic acid, and its three chloro-derivatives. Non-electrolytic acids have no influence on the result: for example, boric acid.

(3) The addition of hypochlorous acid reduces the solubility of chlorine in water, since it acts in virtue of the change, $Cl_2Aq = (HCl + HOCl)Aq$.

Hydrogen chloride, supplying as it does both H and Cl ions, has a very marked influence in dilute solution. This is shown in Fig. 3, p. 228, as an isothermal curve of dissociation. The more concentrated the solution of hydrogen chloride the less the dissociation. For very concentrated solutions of hydrogen chloride we should expect a bimolecular action:

$$Cl_2Aq \rightleftarrows (HCl + HOCl)Aq,$$

and from equation (1)

$$K = \frac{(A - c)^2}{z} \quad . \quad . \quad . \quad (4)$$

or

$$cK = (A - c)(A - c + z),$$

where z denotes the number of hydrogen chloride molecules added to the solution.

When the amount of dissociated chlorine (x) in the solution is exactly equivalent to the amount in combination (y)

$$x, \text{ or } y = \tfrac{1}{2}(\lambda - \chi).$$

From Berthelot's original paper,[1] the conclusion may be drawn that there is a concentration of hydrogen chloride having a maximum

No.	c.c. Thiosulphate.	Gram HCl per 100 gram of solution.	Gram Cl per litre.	t.	p.	Berthelot.	
						Per cent. HCl.	Gram Cl.
1	17·7	2·90	6·0	15·0	759	3	6·0
4	18·9	3·22	6·3	16·3	763	3	6·0
5	21·7	11·53	7·2	16·3	763	—	—
2	23·4	12·19	7·76	15·0	759	—	—
6	31·1	31·24	10·3	16·3	763	33	11·0
3	31·8	32·00	10·55	15·0	759	33	11·0
7	34·9	34·57	11·6	16·3	763	38	17·3
8	36·2	35·90	12·7	16·3	763	38	17·3

[1] The number 17·3 for the weight of chlorine in a 38 per cent. solution of hydrochloric acid attributed above to Berthelot is given in his paper as 7·3. He has recently informed me that this is a misprint. The mistake also occurs in Comey's Dictionary. The experiments in the text were made at the end of 1899 in the attempt to find a point of maximum solubility, before it was found that 7·3 was not the true number.

power of absorption for chlorine. Hydrochloric acid saturated with hydrogen chloride in the cold was used for the strongest solution. The chlorine was passed into the solutions as indicated above. Free chlorine was determined by the usual thiosulphate titration, total chlorine by boiling 10 c.c. of the saturated solution with ferrous sulphate and aqueous potassium hydroxide. The chlorine was then precipitated as chloride from the solution, acidified with nitric acid, and weighed in the usual way. One c.c. of thiosulphate = 0·003319 gram of chlorine.

There is thus no indication of a point of a maximum followed by a diminishing solubility with increasing concentration.

An objection to the preceding method of finding the solubility of chlorine in the stronger solutions might be pointed out. If the current of gaseous chlorine occupies any considerable time, the acid will tend to attain that particular concentration which has a constant composition, and at equilibrium, the chlorine and hydrogen chloride will be distributed according to their partial pressures [1] and the phase rule.

On the Existence of HCl_3 *in Liquid Solution.*

The curve of association indicates the possibility of the existence of some combination of hydrogen chloride and chlorine, possibly stable only in the presence of a great excess of hydrogen chloride, just as the great quantity of chlorine retained by strong solutions led Draper [2] to believe in the existence of a "bichloride of hydrogen," and Berthelot of a "perchloride of hydrogen." [3] In a quite analogous way, Engel found that the solubility of certain chlorides is increased if hydrochloric acid is present in the solution owing to formation of "chlorhydrates." Some of these were isolated; for instance, those of stannic, ferric, cupric, and mercuric chlorides.

The following evidence for the existence of HCl_3 might be cited:

(1). The existence of other well-established tri- and penta-halides.[4]

(2). The partition-coefficient of iodine, between aqueous solutions of potassium iodide and carbon disulphide, leads to the formula $KI{\cdot}I_2$ (Jakowkin).[5]

[1] Perman, Trans., 1895, **67**, 868. [2] Draper, *Phil. Mag.*, 1843, [iii], **23**, 431.

[3] Millon (*J. Pharm.*, 1841, **28**, 299) regarded the yellow liquid remaining when lead chloride is removed by the cooling of the products of the interaction of lead peroxide and concentrated hydrochloric acid according to the equation $PbO_2 + 6HCl = PbCl_2 + 2H_2O + 2HCl_2$. It is now generally believed that the action is $PbO_2 + 4HCl = PbCl_4 + 2H_2O$, although the action $PbO_2 + 5HCl = PbCl_2 + 2H_2O + HCl_3$ appears to be equally probable.

[4] Compare Wells, *Amer. J. Sci.*, 1892, [iii], **43**, 17; Wells and Wheeler, *ibid.*, 1892, **44**, 42, 475.

[5] Jakowkin, *Zeit. physikal. Chem.*, 1894, **13**, 539. Compare Wilderman's $BrHBr_2$, &c., *ibid*, 1893, **11**, 407; Noyes and Seidenstraker, *ibid.*, 1898, **27**, 357.

(3). The increasing solubility of chlorine with increasing additions of hydrogen chloride, and the analogy with Engel's "chlorhydrates."

(4). The heat disengaged by solutions of chlorine in concentrated hydrochloric acid approaches that required for HCl_3, and resembles that required for KI_3 and KBr_3 (Berthelot).

On the Existence of HCl_3 *in Gaseous Solution.*

Evidence for the existence of gaseous HCl_3 was sought by bringing hydrogen chloride and chlorine together in the dark by means of the apparatus devised by Dixon and Harker.[1] A slightly greater contraction occurred, differing from that with hydrogen chloride and air, or with chlorine and air. This might be attributed either to a condensation of the gases on the glass or else to some form of molecular attraction between hydrogen chloride and chlorine.

The only evidence of chemical combination between certain gases is a slight difference between the total volume occupied by the separate and by the mixed gases. It is assumed that if no chemical combination takes place, the mixture will obey Dalton's law of partial pressures, namely, "the pressure exerted by a mixture of gases is equal to the sum of the pressures separately exerted by the several components."

The work of Regnault[2] on mixtures of air with carbon dioxide and with sulphur dioxide; of Andrews[3] on mixtures of carbon dioxide with air and with nitrogen, and of Braun[4] on mixtures of sulphur dioxide and carbon dioxide, sulphur dioxide and hydrogen, sulphur dioxide and nitrogen, hydrogen and carbon dioxide, hydrogen and air, hydrogen and nitrogen, and carbon dioxide and air, shows that Dalton's simple law of addition is not strictly followed.

Dalton's law assumes:

(1) *That each component exerts the same pressure in the mixture that it would if it occupied the space alone.*

To avoid this limitation, Sarrau[5] has proposed to recast Dalton's law somewhat in this form: the specific volume of a mixture of gases is equal to the sum of the specific volumes of the several components. Leduc and Sacerdote[6] find that in this form the law agrees better with the results of their experiments.

[1] Dixon and Harker, *Mem. and Proc. Manchester Lit. Phil. Soc.*, 1890, [iv], **3**, 118.

[2] Regnault, *Mem. de l'Acad.*, 1862, **26**, 256.

[3] Andrews, *Phil. Mag.*, 1876, [v], **1**, 78; *Phil. Trans.*, 1888, **178**, 57.

[4] Braun, *Wied. Ann.*, 1888, **34**, 943.

[5] Sarrau's "Introduction à la Theorie des Explosifs," 25, (1895).

[6] *Compt. rend.*, 1898, **126**, 218, 1853; Leduc's "Recherches sur les gaz," 105, (1898).

D. Berthelot[1] has deduced an expression from van der Waals' equation which gives results in close agreement with experiment for the change of pressure accompanying the mixing of gases, for example:

Calculated increase.	Observed increase.
$CO_2 + N_2O$ ..... 0·00013 atm.	0·00011 atm. (Sacerdote).
$CO_2 + SO_2$ ..... 0·0019 „	0·0018 „ „

These calculations are based on the assumption that the change of pressure which accompanies the expansion of each component of the mixture obeys van der Waals' modification of Boyle's law.

Some interesting examples in which the final pressure is obscured by the dissociation of one of the components of the mixture are treated in a recent paper by Professor Dixon and J. D. Peterkin.[2]

(2). *That the molecules of the different gases exert neither attractive nor repulsive forces on one another.*

According to the kinetic theory, intermolecular attraction will (1) increase the number of collisions between the molecules, (2) cause certain molecules to swerve from their normal rectilinear path, (3) diminish the outward pressure of the gas. The molecules of such a gas are only attracted from within, its volume will therefore be less than that of a gas containing the same number of non-attracting molecules subject to the same external pressure.

It is proved in works on the kinetic theory of gases that for every molecule that loses its motion by collision, another will acquire the same motion by another simultaneous collision. That is to say, unless the attracting molecules during a collision *remain in contact a longer time* than non-attracting molecules, their motion will go on just the same as if there were no collision at all.

Sutherland[3] by assuming that this attractive force varies inversely as the fourth power of the distance between the molecules, has deduced very satisfactory formulæ to explain certain physical properties of gases. For instance, Lord Kelvin and Joule found that the cooling effect produced when a mixture of gases undergoes expansion is not exactly the value calculated on the assumption that there are no attractive forces between the molecules. Sutherland, applying his law of the inverse fourth, obtains results in harmony with experiment. Similarly with the variation of viscosity with temperature, diffusion of gases, &c.

The term av^{-2} in van der Waals' equation is intended to allow for

[1] D. Berthelot, *Compt. rend.*, 1898, **126**, 954, 1030, 1415, 1703, 1857; 1899, **128**, 1159; Leduc, *ibid.*, 1898, **126**, 1859; Van der Waals, *ibid.*, **126**, 1856.

[2] Dixon and Peterkin, Trans., 1899, **75**, 613.

[3] Sutherland, *Phil. Mag.*, 1893, [v], **36**, 507; also 1886, [v], **22**, 81; 1895, [v], **40**, 421.

the effects of the attraction of the molecules when gases undergo certain changes in volume under the influence of a varying pressure.

In a private communication last June, M. D. Berthelot pointed out to me that there is no reason to suppose that the increase of pressure calculated for the mixture of hydrogen chloride and chlorine would differ very much from that for the mixture of carbon dioxide and sulphur dioxide, unless the chlorine exercised some action on the walls of the vessel. Of course this action may to some extent be allowed for by a preliminary saturation of the walls of the vessel with chlorine and comparative experiments with other gases.

Any slight contraction, therefore, which might occur on mixing two gases (say hydrogen chloride and chlorine) cannot be taken as conclusive evidence of a chemical combination (say, formation of HCl_3) until it has been shown that intermolecular forces are inadequate to account for the discrepancy.

III. Thermodynamics of Solutions of Chlorine and Hydrogen Chloride in Water.

If hydrogen chloride be added to a saturated solution of chlorine water in equilibrium with its atmosphere, the chlorine will be redistributed until the potential energy of the system attains a minimum value.

From the properties of the thermodynamical potential, it can be shown that for an increase δv in the amount of HCl present, there will be an increase or a decrease in the amount of chlorine retained by the solution, according as the van't Hoff factor i is less or greater than unity.

J. Willard Gibbs[1] (1876) has shown that the differential of the energy of any material system, subject to gain or loss of energy and of mass, is expressed by the equation:

$$dU = \theta d\phi - pdv + \mu_1 dm_1 + \ldots \mu_n dm_n \quad . \quad . \quad . \quad (1)$$

where U denotes the energy, θ the absolute temperature, Φ the entropy, p the pressure, v the volume, μ the "potential" (Gibbs) or "intensity" (Helm) factor expressing the rate of increase of energy in a reversible increase of unit mass with constant volume energy, namely:

$$\mu = \left(\frac{\partial U}{\partial m_1}\right)_{\theta v m}$$

where m denotes the mass of the body, and as a suffix implies that all other m's in the above formula are constant.

[1] See H. le Chatelier's "Équilibre des Systèmes Chimiques, par J. Willard Gibbs," 54, (1899).

Putting, with Duhem,

$$\Phi = U - \theta\phi + pv \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

we get from (1)

$$d\Phi = -\phi d\theta + vdp + \Sigma\mu dm \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where Φ is clearly a quantity depending only on the parameters describing the particular state of the system, that is, Φ is a complete differential,[1] and

$$\frac{\partial^2\Phi}{\partial x_1 \partial x_2} = \frac{\partial^2\Phi}{\partial x_2 \partial x_1}.$$

Consider now the work (W) gained during an isothermal compression from an initial pressure p_0 to a greater pressure p_1.

$$\int dW = \int_{p_1}^{p_0} vdp \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$
$$= R\theta \int_{p_1}^{p_0} \frac{dp}{p}$$

and, integrating by the aid of the ordinary gas equation,

$$W = R\theta \log_e \frac{p_1}{p_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By differentiation of (2)

$$d\Phi = vdp - \phi d\theta,$$

and since $d\Phi$ is a perfect differential, as in Massieu's well known functions,

$$d\Phi = vdp$$

from (4), therefore

$$\Phi = R\theta \log_e \frac{p_1}{p_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It now remains to show that Φ is a function of the amount of chlorine in solution, or that

$$\Phi = f(\lambda).$$

where λ is the coefficient of solubility.

The extension of the gas laws to dilute solutions by Arrhenius, van't Hoff, and Nernst, enables the various components of the mixture to be expressed as functions of the parameters describing the thermodynamic state of the mixture. Nernst's distribution law allows us to replace the *vapour phase* in the extension of Gibb's equation to Henry's law, by a second *liquid phase*. Let the formula

$$pv = iR\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

[1] Duhem's "Le Potential Thermodynamique," 33, (1895); Trevor, *J. Physical Chem.*, 1897, **1**, 205, 633.

be applicable to dilute solutions of electrolytes, p now representing the osmotic pressure of the dissolved substance, i the isotonic coefficient greater than unity for dissociated substances, that is to say i = a gram-molecule of the substance in solution.

From (2), (6), and (7), if Φ_1 now represent the potential of a given mass, i, of chlorine in dilute solution of hydrogen chloride, Φ_2 that of a more dilute solution, we have at constant temperature,

$$\Phi_2 - \Phi_1 = iR\theta \log_e \frac{p_2}{p_1},$$

where p_1 and p_2 represents the osmotic pressures of the chlorine in the two solutions, hence

$$d\Phi_2 = iR\theta d\log_e \frac{p_2}{p_1}.$$

If the molecular weight i of chlorine in the two solutions is the same, then, by the properties of dilute solutions,

$$\frac{p_2}{p_1} = \frac{C_2}{C_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where C_1 and C_2 are the concentrations of the two solutions $\left(C = \frac{1}{v}\right)$.

We have, therefore, the relation

$$d\Phi = iR\theta d\log_e \frac{C_2}{C_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$
$$= df(\lambda)$$

In words the potential energy of chlorine in dilute solutions of hydrogen chloride is increased by a further addition of the latter gas. By Helmholtz's law, any dynamical system behaves so that the decrease in the potential energy may be a maximum, therefore the solution under these conditions cannot dissolve so much chlorine. If otherwise, the gas is either present in a supersaturated state, that is, in a state of unstable equilibrium (" faux èquilibres," Duhem), or else the stipulation that the molecular weight, i, of chlorine is constant in the different solutions, no longer holds.

In stronger solutions the same solution has phases in which the van't Hoff factor may be

$$i' > 1,\ i'' < 1,\ i = 1.$$

From the earlier part of this paper it follows that there is a considerable variation in the relative values of i for chlorine in the different solutions of hydrogen chloride. For the curve of dissociation $i' > 1$, and for the curve of association $i'' < 1$. In the more dilute solutions of HCl, the relative proportion of $i' > 1$ is the greater, while in concentrated solutions $i'' < 1$ is the larger. At the point of inter-

section of these two curves, we can say no more than that the amount of chlorine (δx) for which $i' > 1$ may be equal to the amount δy for which $i < 1$, or

$$\frac{dx}{dp} = \frac{dy}{dp}, \text{ or } \frac{dx}{dp} - \frac{dy}{dp} = 0.$$

where p is the amount of hydrogen chloride in the solution.

It is then evident from an equation similar to (9) that if, corresponding to HCl_3, $i'' < 1$, the solution will dissolve more chlorine in order that the potential energy may be a minimum, an inference which may be deduced from (1) when the system includes another term $\mu_2 dm_2$.

There is, however, a considerable amount of uncertainty as to what actually takes place in these and all other concentrated solutions. No further progress can be made in a quantitative way until this has been determined. A consistent theory for concentrated solutions is wanting.

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XX.—*On the Nature of Polyiodides and their Dissociation in Aqueous Solution.*

By H. M. DAWSON, Ph.D., B.Sc., late 1851 Exhibitioner.

THE nature of the equilibrium in solutions of potassium iodide containing dissolved iodine has been the subject of frequent investigation and discussion. From the fact that strong solutions of potassium iodide, when saturated with iodine, deposit the latter almost completely on dilution, Dossius and Weith (*Zeit. Chem.*, 1869, 5, 379) concluded that no compound exists in the solution. A similar conclusion was drawn by Baudrimont (*Compt. rend.*, 1860, 51, 287), who found that by means of carbon disulphide the whole of the iodine could be abstracted from a solution of potassium iodide.

Le Blanc and Noyes (*Zeit. physikal. Chem.*, 1890, 6, 385) found that the freezing point of a solution of potassium iodide is but very slightly altered on the addition of iodine; on the other hand, the electrical conductivity of the solution was observed to be considerably smaller. These facts can only be satisfactorily explained by assuming that an additive compound is formed in the solution. By making use of the law regulating the distribution of a substance between two non-miscible solvents to determine the amount of uncombined iodide in the potassium iodide solution, Jakowkin (*Zeit. physikal. Chem.*, 1894, 13, 359; 1896, 20, 19) showed that for dilute solutions, the application of the law of mass

action to the experimental numbers gave results in agreement with the assumption of a dissociation equilibrium represented by the equation,

$$KI + I_2 \rightleftarrows KI_3.$$

Noyes and Seidensticker (*Zeit. physikal. Chem.*, 1898, **27**, 357) finally have shown that in the limiting case where the dilute potassium iodide solution is saturated with iodine the amount of halogen dissolved by solutions of different concentration is also in complete accordance with the above conception of the equilibrium in solution.

In Jakowkin's experiments, a quantity of iodine was shaken up with carbon disulphide and a solution of potassium iodide of known strength, in a stoppered bottle at a constant temperature of 25°, until equilibrium was attained. From the titration of the carbon disulphide layer with sodium thiosulphate, the concentration of the free uncombined iodine in the aqueous layer could be calculated, the total amount of iodine being obtained from the titration of the aqueous layer.

If A denote the iodine concentration in the carbon disulphide layer, c the iodine concentration in the potassium iodide solution, and k the distribution coefficient of iodine for CS_2—H_2O, the fraction of the iodine uncombined is

$$x = \frac{A}{kc}.$$

If, further, v is the volume of the aqueous solution containing one gram-mol. of iodine as titrated by sodium thiosulphate, a the number of gram-mols. of potassium iodide in volume v, and if in the solution we have a dissociation equilibrium which can be represented by the equation

$$KI + I_2 \rightleftarrows KI_3,$$

then, neglecting electrolytic dissociation, there will be present in volume v, $(1-x)$ gram-mols. of the complex compound and $(a-1+x)$ gram-mols. of potassium iodide. Application of the law of mass action to the above equation leads to the equilibrium constant,

$$k = \frac{(a-1+x)x}{v(1-x)}.$$

Jakowkin found that the expression thus obtained for k is constant, provided the concentration of the iodine is not very great.

On account of the electrolytic dissociation, the equilibrium in solution is, however, not quite so simple as the above equation would suggest, and in order to set up a strictly applicable formula this dissociation must be taken into account. Assuming that a compound of the formula KI_3 exists in the solution, and that this undergoes electrolytic dissociation with the formation of I_3 ions, then if the I_3 ion is one of the components of the equilibrium in which the free molecular iodine

takes part, we may represent the equilibrium in solution by the following dissociation isotherms:

$$(1).\quad KI_3 \rightleftarrows \overset{+}{K} + \overset{-}{I}_3.$$

$$(2).\quad KI \rightleftarrows \overset{+}{K} + \overset{-}{I}.$$

$$(3).\quad \overset{-}{I}_3 \rightleftarrows \overset{-}{I} + I_2.$$

Let k_1 and k_2 denote the dissociation constants of the states of equilibrium represented by equations (1) and (2), and suppose that the degree of electrolytic dissociation of the triiodide and of the iodide in their common solution is y and z respectively. If, further, v, a, and x have the signification previously assigned to them, the constant, k, of the dissociation equilibrium in which, according to the above formulation, the uncombined iodine takes part is:

$$k\frac{y(1-x)}{v} = \frac{z(a-1+x)x}{v^2}, \text{ or}$$

$$k = \frac{z}{y}\frac{(a-1+x)x}{v(1-x)} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

From this equation y and z might be eliminated by writing down the values for the dissociation constants k_1 and k_2. Since the concentrations of undissociated KI_3 and KI are $\frac{(1-y)(1-x)}{v}$ and $\frac{(1-z)(a-1+x)}{v}$, and those of the $\overset{+}{K}$, $\overset{-}{I}_3$, and $\overset{-}{I}$ ions respectively $\frac{y(1-x)+z(a-1+x)}{v}$, $\frac{y(1-x)}{v}$, and $\frac{z(a-1+x)}{v}$, we obtain for k_1 and k_2 by application of the law of mass action to the dissociation equilibria, the following expressions:

$$k_1 = \frac{y[y(1-x)+z(a-1+x)]}{(1-y)v} \qquad k_2 = \frac{z[y(1-x)+z(a-1+x)]}{(1-z)v}.$$

The resulting expression for k would obviously only contain the electrolytic dissociation constants k_1 and k_2 in addition to the factors x, v, and a, which are determined directly by experiment.

The ordinary method of determining the electrolytic dissociation constant by conductivity measurements fails, however, in the case of strong electrolytes. This cannot be taken as evidence or proof of the non-existence of such a constant in these cases, since it is a direct consequence of the application of the law of mass action, and the dissociation formulæ not only result from the application of molecular kinetic conceptions, but rest on the sure basis of thermodynamics. It must rather be inferred that the ratio of the molecular conductivities λ_v/λ_∞ does not give the true value of the degree of dissociation

in the case of strong electrolytes. According to Jahn (*Zeit. physikal. Chem.*, 1900, **33**, 545), the reason of this is to be found in the experimental fact that in the case of strongly dissociated substances, the ionic mobility not only depends upon the intrinsic nature of the ions, but also upon the concentration of the solution. This is the case even for very dilute solutions. Arrhenius (*Zeit. physikal. Chem.*, 1899, **31**, 197) attributes the increase in the value of the Ostwald constant with increasing concentration of the solution to the stimulating action of the ions themselves in promoting electrolytic dissociation, comparing it with the action of neutral salts in increasing the dissociation of weak acids. Until the anomalous behaviour of strong electrolytes is satisfactorily explained, the values of the dissociation constants of salts cannot be determined. The empirical constant of Rudolphi or van't Hoff has no theoretical signification and cannot be regarded as a dissociation constant.

For the compounds under consideration in this paper the values of k_1 and k_2 are therefore not known, and the general equation for the equilibrium in the haloid salt solution cannot be directly subjected to the test of experiment. The experimental results can, however, be applied in an inverse manner to enable conclusions to be drawn with regard to the nature of the components taking part in the equilibrium. If we assume that the triiodide and the iodide in their common solution are electrolytically dissociated to the same extent ($y = z$), which is equivalent to the assumption that the dissociation constants k_1 and k_2 are equal, the formula (1) for k reduces to the simpler form

$$k = \frac{(a - 1 + x)x}{v(1 - x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is identical with the dissociation formula set up by Jakowkin (*loc. cit.*)

The experiments of Jakowkin, carried out at 25°, show that for solutions up to 1/4 normal in regard to potassium iodide and to 1/10 normal with respect to iodine, the values of k calculated from equation (2) are very constant. In order to confirm these results and so justify any conclusions drawn from them and further to determine the influence of temperature on the dissociation, a series of experiments was carried out similar to those of Jakowkin but at a different temperature. The temperature chosen was 13·5°, the lowest which could be conveniently maintained in the laboratory for considerable periods of time. For the calculation of the degree of dissociation of the polyhaloid compound, it was necessary to know the distribution ratio of iodine between carbon disulphide and water at 13·5°. Three experiments were carried out at 15° (the ratio at this temperature being required for another investigation) the values obtained being 616·8, 619·6, and 624·0, mean = 620. The value obtained by Jakowkin at 25° for the

smaller concentrations of iodine, such as were used in my experiments, was 585. By extrapolation, the value of the distribution ratio at 13·5° obtained is 625. The distribution coefficient varies considerably therefore with the temperature, decreasing by about 0·6 per cent. for a rise of 1°.

The experiments to confirm the validity of equation (2) were carried out as follows. About 30 c.c. each of carbon disulphide and of potassium iodide solution of known strength were introduced into a stoppered cylindrical separator, a weighed quantity of iodine added, and after shaking for five minutes and allowing to stand at 13·5° until the two layers had completely separated, the concentration of the iodine in each was determined. The small changes resulting from the mutual solubility of the two media, and the small influence of the presence of dissolved salt in the aqueous phase on the value of the distribution coefficient of the iodine, could be neglected. The following tables contain the experimental data and the calculated values of k from equation (2): c is the iodine concentration in the aqueous solution, A that in the carbon disulphide; x the fraction of uncombined iodine in the aqueous solution $= A/625c$, v the volume of the aqueous solution containing 1 gram of iodine and a the molecular ratio KI/I_2.

c.	A.	x.	v.	a.	k.
1/8 N potassium iodide:					
1·255	6·627	0·008449	202·1	25·27	0·001021
2·283	12·69	0·008893	111·1	13·89	0·001042
4·425	25·58	0·009249	57·33	7·166	0·001006
7·185	48·10	0·01071	35·31	4·414	0·00105
1/4 N potassium iodide:					
1·229	3·205	0·004173	206·4	51·60	0·001027
2·154	5·751	0·004272	117·8	29·45	0·001037
4·231	11·39	0·004306	59·96	14·99	0·00101
4·313	11·63	0·004315	58·82	14·70	0·00101
6·469	18·31	0·004529	39·22	9·805	0·001021
8·898	25·89	0·004655	28·51	7·128	0·001005
12·66	39·68	0·005015	20·04	5·01	0·001008
N potassium iodide:					
5·731	3·657	0·001020	44·27	44·27	0·0009984
11·10	7·062	0·001018	22·86	22·86	0·0009744
19·14	12·68	0·00106	13·26	13·26	0·0009811
54·63	35·94	0·001052	4·644	4·644	0·000827

The value of k as calculated from equation (2) is constant provided the concentration of the halogen is not too great, although there appears to be a slight gradual decrease as the concentration of the potassium iodide increases, which can probably be explained by the influence of the dissolved salt on the value of the distribution coefficient, which has been assumed to be constant. The mean value of the constant (0·001015) is, however, much smaller than that determined by Jakowkin at 25°, namely, 0·00138. That this difference is merely due to the difference of temperature is shown by the result of two experiments made with 1/8 normal potassium iodide at 25°, the values of k obtained being 0·001361 and 0·001351, which agree with the constant determined by this author. Even with 1/160 normal potassium iodide solutions, k at 25° retains the same value as at the higher concentrations.

The following numbers show the influence of temperature on the degree of chemical dissociation of the polyhaloid compound, the percentage of uncombined iodine at the concentrations given in the table having been interpolated from curves representing the experimental data :

Concentration of iodine.	Degree of dissociation of the polyiodide at 13·5°	25°
1/4N potassium iodide $\frac{1}{128}$ molecular.	0·439 per cent.	0·575 per cent.
,, ,, $\frac{1}{64}$,,	0·452 ,,	0·592 ,,
,, ,, $\frac{1}{32}$,,	0·481 ,,	0·628 ,,
1/8N ,, ,, $\frac{1}{128}$,,		
,, ,, $\frac{1}{64}$,,	0·905 ,,	1·16 ,,
,, ,, $\frac{1}{32}$,,	0·97 ,,	1·25 ,,
	1·14 ,,	1·44 ,,

The dissociation of the polyhaloid compound obviously increases with rise of temperature, the relative increase for a rise of temperature from 13·5° to 25° being in each of the above cases about 25 per cent.

From the fact that the simplified equation (2), represents the experimental results within the above limits in such a satisfactory manner, it may be concluded that the assumption made in the deduction of this equation from the general one is justifiable. In accordance with this assumption, namely, that the degree of electrolytic dissociation of iodide and triiodide in the solution containing both is the same, potassium triiodide must be considered as a salt the electrolytic dissociation constant of which is the same as that of potassium iodide ; its character is therefore that of a normal salt of potassium. It should be noted that equation (1), would also represent the experimental results with the same amount of exactitude if instead of $y/z=1$, we assumed $y/z=k'$ any constant, but such a

relationship between the degrees of dissociation of electrolytically dissociating compounds for varying relative and absolute concentrations is not known.

The result thus arrived at regarding the nature of potassium triiodide is perhaps what might have been expected, if the latter be regarded as a substance having the character of a true salt corresponding to an acid of the formula HI_3. The case of the corresponding acid is, however, quite different. *A priori*, it is impossible to say whether this acid belongs to the weak acids, to the half electrolytes, or the strong acids. For the equilibrium in a solution of hydriodic acid containing iodine, dissociation isotherms can, however, be written down analogous to those employed in the case of the potassium iodide solution, and the application of the law of mass action leads as before to the equilibrium constant $k=\frac{z}{y}\frac{(a-1+x)x}{v(1-x)}$ for the reaction in which the free molecular iodine is supposed to take part, y being the degree of electrolytic dissociation of HI_3 and z that of the HI in the same solution.

If the two halogen acids are not of the same order of magnitude in respect of their chemical affinities, the ratio z/y will vary very considerably with varying concentration of the solution and with the relative masses of the two compounds. If, as before, however, we assume that the electrolytic dissociation constants of HI_3 and of HI are equal, then $y=z$, and the equation reduces to the simpler form represented by equation (2).

A series of iodine distribution experiments similar to those previously described, was carried out with solutions of hydriodic acid. The results are contained in the table on page 245, the numbers in the several columns corresponding to those in the previous table for solutions of potassium iodide.

As was found by Jakowkin at 25°, the value of k calculated from the simple equation remains constant within the limits of experimental error for all the concentrations investigated. In agreement with his results also, the equilibrium constant for the acid solution is somewhat less than that for the salt solution, the numbers at 13·5° being 0·00098 and 0·001015 and at 25° 0·00134 and 0·00138 respectively.

The constancy of k shows that the assumption made in the deduction of the simple formula is justified. The electrolytic dissociation constant of HI_3 is therefore of the same order of magnitude as that of hydriodic acid; in other words, the compound HI_3 belongs to the group of strong acids, and in aqueous solution at moderate dilutions is (apart from the chemical dissociation) almost completely dissociated into its ions $\overset{+}{H}$ and $\overset{-}{I_3}$.

v.	A_v	x.	v.	a.	$k=\frac{(a-1+x)x}{(1-x)v}$.
1/8 *N* hydriodic acid:					
0·730	3·662	0·008026	347·6	43·45	0·0009888
2·260	11·66	0·008254	112·2	14·02	0·0009658
2·987	16·14	0·008646	84·94	10·62	0·0009878
5·001	28·84	0·009227	50·73	6·341	0·0009830
7·615	43·21	0·01013	33·32	4·165	0·0009754
1/16 *N* hydriodic acid:					
0·6246	8·128	0·01609	394·8	24·68	0·0009812
2·046	22·11	0·01729	124·0	7·75	0·0009602
1/32 *N* hydriodic acid:					
0·5815	11·74	0·0323	436·2	13·63	0·000969
0·864	18·32	0·03394	293·6	9·175	0·0009822

According to the theory of Abegg and Bodländer (*Zeit. anorg. Chem.*, 1899, **20**, 453), every complex ion may be supposed to consist of a simple ion combined with a neutral component. As a result of this formation of a complex ion, the electro-affinity—that is, the affinity of the atom or atomic group for the electric charge—of the ion is increased. The greatest tendency towards the formation of such complex ions by addition of a neutral group of atoms is exhibited by weak ions, that is, those of small electro-affinity. In the case of the complex ion $\bar{I}_3$, the neutral component I_2 has the same chemical composition as the simple ion $\bar{I}$, analogous to which we have the complex divalent mercurous ion $\overset{++}{Hg}_2$, which results from the mercuric ion $\overset{++}{Hg}$ by addition of a neutral atom of mercury. In the case of weak ions, the formation of complex ions has an enormous effect in increasing the electro-affinity, compare the $\bar{\bar{S}}$ ion with the $\bar{\bar{S}}O_4$ ion, but in the case of strong ions which, as a rule, have a much smaller tendency to form complex ions, the increase is relatively small, compare the $\bar{Cl}$, $\bar{Cl}O_3$, and $\bar{Cl}O_4$ ions. The electro-affinity of the latter ions is not very different. The iodine ion $\bar{I}$ is already a strongly electronegative ion, and the formation of a complex ion by the addition of a molecule of iodine would not be expected to produce any remarkable increase in the electronegative character. The result obtained above regarding the relative degrees of dissociation of hydrogen iodide and hydrogen triiodide is in harmony with this conclusion.

With regard to the velocity of migration of the complex ion I_3 under the influence of a difference of potential, some light may be obtained from the measurements of Le Blanc and Noyes (*loc. cit.*) of the conductivity of potassium iodide solutions containing iodine.

The following numbers are taken from their paper, v denoting the volume in litres containing one gram-molecule of KI, the molecular conductivities having been multiplied by 10^7 :

v.	μ_v (KI).	μ'_v (KI + 4/10I)	Percentage diminution of μ'_v compared with μ_v.
2	112·7	101·6	9·9
8	121·1	110·4	8·8
32	128·2	117·0	8·7
54	130·7	121·5	7·0
128	133·2	125·4	5·8
256	135·4	128·9	4·8

At all the concentrations investigated, the molecular conductivity is considerably diminished on the addition of iodine. The migration velocity of the complex ion would appear to be smaller than that of the simple ion. This diminution of the velocity of the ion with increasing complexity is in accordance with the regularities observed regarding the dependence of the velocities of organic acid ions on the number of the atoms contained in them when this number does not exceed a certain limit represented by about twelve atoms.

In connection with the views brought forward in this paper, some older observations of Johnson (this Journ., 1877, **31**, 249) regarding the nature of potassium triiodide are of interest. By slow evaporation of a potassium iodide solution containing dissolved iodine over sulphuric acid, he found that lustrous, dark blue prismatic crystals were deposited which had the composition required by the formula KI_3. The specific gravity of these crystals was found to be 3·498, from which the atomic volume of the triiodide = 120·1. Now the atomic volume of potassium + three times the atomic volume of iodine = 122·2, whereas the atomic volume of potassium iodide + twice the atomic volume of iodine = 105·6, "so that it appears that the triiodide of potassium does not consist of a molecule of potassium iodide united with a molecule of iodine, but of an atom of potassium united with three atoms of iodine without condensation."

The existence of a large series of polyhalogen compounds of cæsium and rubidium, in which the metals appear to be ter- and quinquevalent, has been shown in recent years by Wells (*Zeit. anorg. Chem.*, 1892, **1**, 85) and Wheeler (*Zeit. anorg. Chem.*, 1892, **1**, 442 ; **2**, 255), and by Erdmann. Without entering into the merits of the distinction, the admission, by a large number of chemists, of the possi-

bility of differentiation between so-called 'molecular' and 'atomic' compounds, forces upon us the question as to whether these polyhaloid derivatives of cæsium and rubidium belong to the first or to the second class. If the analogy between these compounds and the less stable potassium triiodide and the evidence in favour of the latter being an 'atomic' compound be considered, then there are grounds for the conclusion that at any rate the trihaloid derivatives of cæsium and rubidium are also 'atomic' as opposed to 'molecular' compounds.

THE YORKSHIRE COLLEGE,
LEEDS.

XXI.—*The Decomposition of Chlorates. Part III. Calcium Chlorate and Silver Chlorate.*

By WILLIAM H. SODEAU, B.Sc.

PURE calcium sulphate, silver sulphate, and barium chlorate were prepared, and by carefully balancing the barium salt with the sulphates, pure calcium and silver chlorates were respectively obtained; these chlorates were subsequently recrystallised. When employing silver sulphate the barium chlorate should be added little by little, never exceeding the amount required to precipitate the sulphate already in solution, as an excess practically stops the reaction.

Calcium Chlorate.

By heating at 160—165°, the crystals of the dihydrate $Ca(ClO_3)_2,2H_2O$ were slowly rendered anhydrous. The product, which was very deliquescent, contained only a faint trace of chloride and was neutral to methyl-orange; unlike commercial specimens, it was free from magnesium. Potilitzin (compare Abstr., 1892, 62, 1275) has studied the decomposition under atmospheric pressure with reference to the formation of a small proportion of perchlorate and the relation of temperature to rate of decomposition.

Examination of the Decomposition Products.—The solid residue from the partial decomposition of 1 gram of chlorate was dissolved in water with the addition of a little methyl-orange, some *N*/50 nitric acid was then added, and the slight excess titrated back with *N*/50 soda. The amount of calcium oxide or of liberated chlorine having been thus ascertained, the neutral liquid was diluted to 50 c.c., and the calcium chloride determined by titrating two 10 c.c. portions with

Doyle 1971 here!

$N/10$ silver nitrate, using potassium chromate as an indicator. To test for peroxide, 20 c.c. were treated with 0·2 c.c. of $N/100$ permanganate and a little $N/50$ nitric acid; the pink colour was not discharged even after standing for some minutes, and titration with $N/100$ thiosulphate, after adding potassium iodide and starch, indicated no appreciable reduction of the 0·2 c.c. of permanganate. Had the whole of the oxide been present as CaO_2, 1·0 to 7·3 c.c. would have been bleached. The oxide present in the residue must, therefore, be CaO (probably as oxychloride), but it may be formed by reduction of the peroxide, as calcium chlorate tends to be converted into perchlorate.

The numerical results stated in Table I (p. 249), were calculated from the analyses of the residues, but accidental errors were guarded against by observing the loss of weight, volume of oxygen, and (in decompositions conducted under atmospheric pressure) the amount of iodine liberated from potassium iodide. The potassium iodide did not become alkaline, hence the gas contained no appreciable amount of ozone or of oxides of chlorine.

As in previous papers, the chlorine has been stated per 100 parts contained in the weight of chlorate actually decomposed.

Decomposition under varied Conditions.—The chlorate in portions of 1 gram was decomposed in bulbs of 30 mm. diam. blown at the end of soda glass tubes of 8 mm. bore (placed in a bath of fusible metal together with a thermometer); in other respects, these experiments were conducted in the same manner as the decompositions of lead chlorate (Trans., 1900, **77**, 718).

Calcium chlorate undergoes fusion at the beginning of the decomposition, and its great tendency to spirt has rendered it uncertain whether reduction of pressure affects the rate of decomposition. A slight retardation observed on reducing the pressure to 4 mm. in experiments 155 and 156 is probably explicable by the fact that the average temperature as well as the pressure must have been reduced, for under 4 mm. the greater part of the chlorate left the lower half of the bulb and a portion formed a broad ring in the 8 mm. tube.

In the slow decompositions, the temperature of the bath was about 295—320° during the greater part of the time, being slowly raised in order to render the rate fairly uniform.

In experiments 157 and 160 the average amount of chloride present during the decomposition was more than double that in experiments 155*a* and 156*a*, yet rather less free chlorine was obtained in the two former experiments; this appears to show that no appreciable amount of chlorine was displaced from previously formed chloride, for otherwise the proportion should have been much greater in experiments 157 and 160.

Experiments 155*b* and 156*b* were similar to 157 and 160, except as

regards pressure; their mean gives 0·58 per cent. of free chlorine at atmospheric pressure as compared with 0·54 per cent. under 4 mm. pressure. Since reduction of pressure caused no increase of free chlorine, there was no appreciable action between chlorine and calcium oxide, for this would have varied with the concentration (or pressure) of the gas.

In experiments 154 and 158 the greater part of the decomposition

TABLE I.—*Calcium chlorate.*

No.	Duration (minutes).	Proportion decomposed (per cent.).	Pressure.	Chlorine (total in decomposed portion =100).		Mols. chloride / Mols. oxide.
				Free.	As chloride.	
154	About 0·1	95·9	1 atmosphere	2·35	97·65	41·5
158	,,	94·1	,,	2·02	97·98	48·4
159	(?)	78·5	,,	1·52	98·50	65
155*a*	120	31·8	4 mm.	0·90	99·10	110
156*a*	140	28·3	,,	0·95	99·05	104
157	105	63·2	4 mm.	0·56	99·44	179
160	100	67·7	,,	0·52	99·48	191
155*b*	120	76·0	1 atmosphere	0·51	99·49	197
156*b*	140	80·5	,,	0·66	99·34	151

The "proportion decomposed" under 4 mm. pressure would doubtless be much higher if ascertained for the portion remaining at the bottom of the bulb.

took place in a few seconds, the *thermometer bulb* being then at about 355°; rapid decomposition greatly increased the proportion of free chlorine, the mean being 2·2 per cent. as compared with 0·58 in slow decomposition. Experiment 159 gave a lower result because the bath was heated too slowly and a fair amount of the chlorate decomposed before the rush occurred.

The further significance of these results is discussed in the last section of the paper.

Silver Chlorate.

This chlorate is anhydrous and sparingly soluble. After drying at 100° it dissolves in water to a practically clear solution neutral to methyl-orange. When the salt is wrapped in paper, a tap with a hammer readily produces an explosion, but on a clean anvil I have not

been able to explode it by a blow. If rapidly heated in a glass tube, it explodes with a yellow flash and sharp report when the thermometer in the bath has reached a temperature of about 345°, the increase in the rate of decomposition giving very little warning of the approach of the explosion. Analyses of the solid residues resulting from three such experiments showed that the proportions of free chlorine were respectively 5·1, 8·7, and 6·2 per 100 parts of chlorine present in the substance. Some metallic silver was formed, probably because the temperature rose beyond that at which silver oxide ceases to be even moderately stable.

Silver chlorate undergoes slow decomposition at about the same temperature as calcium chlorate and with far more difficulty than lead chlorate (*loc. cit.*), yet the violence of its decomposition when rapidly heated is much greater than is the case with either of these chlorates.

Slow Decomposition under Varied Conditions.—The mode of working resembled that adopted in the case of calcium chlorate (p. 247) except that plain tubes of 18 mm. bore, sealed at one end, were substituted for bulb tubes. By employing potassium iodide solution, the gas was shown to be free from ozone and oxides of chlorine, as in the case of other chlorates. The solid residue was completely soluble in ammonia and hence contained no appreciable amount of metallic silver, although, for example, a tenth of the residue consisted of silver oxide. Each residue was thoroughly disintegrated in $N/10$ nitric acid; after standing for twenty-four hours methyl-orange was added and the excess of acid titrated with $N/50$ soda; the difference gave the amount of oxide in the residue and hence the amount of chlorine remaining free. The residual silver chloride * was weighed in order to determine the "chlorine as chloride," and the filtrate titrated with $N/10$ sodium chloride as a check upon the other results. The "proportion decomposed" was calculated from the sum of oxide and chloride.

Variation of pressure did not markedly affect the rate of decomposition, but it will be seen from Table II. (p. 251) that, as in the case of lead chlorate (*loc. cit.*) each decrease of pressure caused an increase in the amount of chlorine remaining free. There was, therefore, considerable secondary action between the chlorine and the silver oxide, this being lessened on diminishing the concentration (that is, pressure) of the gas. The residues obtained under atmospheric pressure were practically white, whilst those formed under reduced pressure were dark brown, owing to the large proportion of oxide.

In experiment 168 there was a second tube in which the chlorate was

* When this was dissolved in ammonia and reprecipitated with nitric acid no silver remained in solution, hence the whole of the silver oxide had been dissolved by the standard acid.

decomposed under atmospheric pressure whilst a current of dry air was led to the bottom of the tube and up through the substance; the volume of air was nearly fifty times that of the gas evolved, and the proportion of free chlorine was 2·3 per cent.—about ten times that ordinarily obtained under atmospheric pressure but only about a third of that found under 20 mm. pressure. The silver chlorate fused and remained fairly liquid until near the stage at which these decompositions were stopped; this will explain the relative inefficiency of the air current, the gas in many of the bubbles doubtless escaping dilution. In experi-

TABLE II.—*Silver chlorate.*

No.	Duration (minutes).	Proportion decomposed (per cent.)	Pressure.	Chlorine (total in decomposed portion = 100).		Equivs. chloride. / Equivs. oxide.
				Free.	As chloride.	
161*b*	90	78·5	1 atmosphere	0·15*	99·85	670*
163*b*	70	71·8	,,	0·14*	99·86	690*
165*b*	130	50·0	,,	0·24*	99·76	420*
166*b*	140	63·7	,,	0·25*	99·75	400*
161*a*	90	88·5	about 20 mm.	7·76	92·24	11·9
163*a*	70	87·8	20 mm.	6·75	93·25	13·8
172	110	73·2	6 ,,	16·8	83·2	4·96
167	120	69·6	4 ,,	18·4	81·6	4·44
165*a*	130	72·4	$3\frac{3}{4}$,,	19·1	80·9	4·24
168	110	60·4	3 ,,	21·1	78·9	3·74
166*a*	140	68·4	$2\frac{1}{2}$,,	22·6	77·4	3·42
164	(Explosion).		1 atmosphere	5·1	94·9	18·5
169	,,		,,	8·7	91·3	10·4
170	,,		,,	6·2	93·8	15·1

* In the numbers marked with an asterisk, only the first figure is really significant.

ments 167 and 172 there were comparison tubes each containing 1 gram of silver chlorate together with half a molecular proportion of well washed dry silver chloride, this addition more than doubling the average amount of chloride present. The chloride had no marked influence upon the rate of decomposition, but slightly more chlorine remained free, the (total) amounts being 20·9 per cent. at 4 mm., and 18·1 per cent. at 6 mm. As silver chloride appears to dissolve in the fused chlorate, the increase, which was about the same as that caused by lowering the pressure to the extent of 1 mm., is sufficiently accounted for by

the decrease in reabsorption brought about by the dilution of the silver oxide. The conclusion is therefore drawn that silver chloride is practically unaffected by decomposing silver chlorate and hence that no appreciable proportion of the free chlorine accompanying the oxygen has been displaced from previously formed chloride.

Duration and average temperature of decomposition did not vary to any very great extent in the series of experiments at present under consideration, and increase of duration was necessarily coupled with decrease of temperature, so that such variations as occurred tended to compensate for each other as regards the secondary action between chlorine and silver oxide, hence this action was mainly a function of the pressure of the gas. Plotting the observed pressures (ranging from 2·5 to 760 mm.) as ordinates and taking as abscissæ the number of equivalents of silver chloride to one equivalent of oxide (Table II., last column), it was noticed that all points lay close to a straight line, as might have been expected from theoretical considerations. On producing this line, it was found to cut the axes in the points (1·8, 0 mm.) and (0, −3 mm.) respectively. It thus appears that if a perfect vacuum could be maintained above the liquid, the observed ratio of chloride to oxide would be 1·8 : 1, or in other words 36 per cent. of the total chlorine would be obtained in the free state.*

To eliminate reabsorption, it is, however, necessary to put the average pressure in the *bubbles* equal to zero. Under reduced pressure, the bubbles are large at the surface, hence their (unknown) average internal pressure caused by surface tension cannot be great. The pressure axis is cut at −3 mm., hence the supposition that the chlorate first of all decomposes entirely into oxide, chlorine, and oxygen requires that the average internal presure should be 3 mm.

Summary of Results.

Considerations resembling those given in Parts I. and II. (Trans., 1900, 77, 137, 717) will apply to calcium and silver chlorates. It follows that during the slow decomposition of the chlorates of (potassium †), barium, calcium, lead, and silver, the whole of the free chlorine is produced directly, that is, it is not displaced from previously formed chloride, and the primary cause of the production of oxygen and chlorine is the occurrence of two simultaneous and independent reactions which may be represented by the equations $2M(ClO_3)_2 = 2MCl_2 + 6O_2$ and $2M(ClO_3)_2 = 2MO + 2Cl_2 + 5O_2$ ‡ where M is written for Ca, Ag_2, &c.

* This mode of elimination could not be employed with lead chlorate, as decrease of pressure necessitated a considerable increase of temperature.

† Chlorine vanishingly small.

‡ Lead chlorate yields PbO_2 instead of PbO.

With calcium chlorate, the "chloride" decomposition proceeds at about 180 times the rate of the "oxide" decomposition, and the free chlorine has no appreciable action on the oxide or oxychloride; this chlorate resembles barium chlorate (*loc. cit.*, p. 138), the main difference being that the calcium salt yields much more free chlorine. In the case of silver chlorate, the velocity of the "chloride" is less than 1·8 times that of the "oxide" decomposition (hence more than 36 per cent. of the total chlorine is first liberated), but simultaneously the reaction $Ag_2O + Cl_2 = 2AgCl + O$ proceeds to an extent determined by the conditions, all but about 0·2 per cent. of the total chlorine recombining under atmospheric pressure. The latter results resemble those obtained with lead chlorate (*loc. cit.*, p. 717), but are more striking although less complete. As silver chlorate resembles the barium and calcium salts in fusing during decomposition, the proof of the absence of any recombination of chlorine during the decomposition of the two latter chlorates is supported by the behaviour of this chlorate in a more satisfactory manner than by the results obtained with (non-fusing) lead chlorate. The "chloride" decomposition evolves much heat, whilst it is practically certain that the "oxide" decomposition is an endothermic reaction, and hence might be expected to gain upon the "chloride" decomposition when the temperature is greatly raised, as in violent decomposition. This will account for a much larger proportion of free chlorine being obtained when calcium chlorate is rapidly decomposed; in the case of silver chlorate, the increase may partly depend also upon the alteration in the conditions under which the chlorine acts upon the silver oxide.

Lead chlorate and silver chlorate yield large quantities of oxide on decomposition, although in either case the oxide has a low heat of formation, and is rapidly attacked by the chlorine simultaneously produced; this accords well with the accepted view of the structure of the chlorate molecule, namely, that the metal is joined directly to oxygen. The decomposition of the chlorates of calcium, barium, and potassium has, however, been shown to consist almost entirely (and that of lead chlorate to the extent of about 12 per cent.) of the direct production of chloride and oxygen without the intermediate formation of oxide. This would appear to show either that these chlorates are transformed at high temperatures into isomerides in which the metal is directly attached to chlorine, or else that the main decomposition is a reaction taking place between two molecules, the chlorine of one uniting with the metal of the other.

XXII.—*The Action of Ethylene Dibromide on Xylidine and ψ-Cumidine.*

By Alfred Senier and William Goodwin.

Among the reactions announced by Hofmann in his classical researches on amines is that between ethylene dibromide and aniline whereby important bases are formed each of which has been fruitful as leading to subsequent discovery. Of these, two are especially notable, namely, diphenylethylenediamine and diphenyldiethylenediamine. The latter is now called diphenylpiperazine, a name suggested by Merz and Mason (*Ber.*, 1887, **20**, 267), which shows in a happy manner its relation to other heterohexacyclic compounds. The following experiments were undertaken with the object of applying this reaction to the production of the related xylyl and cumyl bases, and of obtaining from them derivatives homologous with those which Mills has described (Trans., 1900, **77**, 1020). We have also endeavoured to extend this reaction with the view of preparing methylenediamine derivatives and have succeeded in obtaining a series of well crystallisable methylene compounds. The study of these as well as their behaviour with phenylcarbimide we propose to continue.

Dixylylethylenediamine, $C_2H_4(NH\cdot C_6H_3Me_2)_2$.

Pure xylidine of commerce (b. p. 212°) which consists chiefly of the unsymmetrical meta-isomeride was employed. Four mols. of the base were brought together with 1 mol. of ethylene dibromide in presence of sufficient sodium carbonate to neutralise the hydrogen bromide set free. In order to moderate the reaction, the base was mixed with the sodium carbonate in a flask fitted with a reflux condenser and the ethylene dibromide gradually added through the latter. The reaction was completed by heating in an oil-bath for three hours at 145—150°, the mass being frequently shaken. The contents of the flask were shaken into cold water, which removed the sodium salts and left a soft, resinous mass. This was washed with cold rectified spirit and afterwards extracted with the hot solvent. From this solution on cooling, white feathery crystals separated; after recrystallising three times from absolute alcohol they melted at 74—75°. On analysis:

0·2094 gave 0·6136 CO_2 and 0·1710 H_2O. C = 80·56; H = 9·06.

$C_{18}H_{24}N_2$ requires C = 80·59; H = 8·95 per cent.

Dixylylethylenediamine nitrate, $C_2H_4(NH\cdot C_6H_3Me_2)_2,2HNO_3$, was prepared by adding dilute nitric acid to an alcoholic solution of the

base. Rise of temperature was prevented by surrounding the vessel containing the solution with cold water. On standing, small colourless needles were deposited which, after washing with water, melted at 165°. These were recrystallised from dilute alcohol and then melted at 166°. On analysis:

0·3982 gave 47·6 c.c. moist nitrogen at 13° and 747·5 mm. N = 13·91.
$C_{18}H_{24}N_2,2HNO_3$ requires N = 14·21 per cent.

Dixylylethylenediamine Platinichloride, $C_2H_4(NH\cdot C_6H_3Me_2)_2,H_2PtCl_6$, separates as bright yellow, glistening crystals when a solution of platinic chloride in alcohol is added to an alcoholic solution of the base. The salt was dried at 130°, and, on analysis:

0·0542 gave 0·0157 Pt. Pt = 28·96.
$C_{18}H_{24}N_2,H_2PtCl_6$ requires Pt = 28·79 per cent.

Dixylylethylenediamine Mercurichloride, $C_2H_4(NH\cdot C_6H_3Me_2)_2,HgCl_2$, is deposited as pale yellow, well-formed crystals by allowing a mixture of alcoholic solutions of the base and mercuric chloride, in molecular proportion, to stand for 24 hours; it may be recrystallised from dilute alcohol. The melting point is not definite, but is reached at about 118°. On analysis, 34·3 per cent. of Hg was obtained, whilst the formula requires 37·1 per cent. There can be no doubt, however, that the formula given is the correct one, for it is very difficult to obtain these mercurichlorides without admixture of either mercuric chloride or the base.

Tetranitrodixylylethylenediamine, $C_2H_4[NH\cdot C_6H(NO_2)_2Me_2]_2$, was obtained by treating a solution of the base in glacial acetic acid with an excess of concentrated nitric acid. On warming, a brisk reaction commenced, which, for its completion, required the application of heat. Pale yellow crystals made their appearance, increasing in quantity as the liquid cooled. The crystals were collected and washed, first with acetic acid and then with water. After drying, they melted at 220°. On analysis:

0·3542 gave 57·2 c.c. moist nitrogen at 12° and 752·5 mm. N = 18·98.
$C_{18}H_{20}O_8N_6$ requires N = 18·75 per cent.

After the separation of the tetranitro-derivative, the solution, on addition of water, deposited a small quantity of an orange-red, semi-plastic mass, which became crystalline and melted at 52—53°. There was not sufficient of the substance to enable a further study to be made of it, but from the analogous experience of Mills (Trans., 1900, 77, 1021), in the case of ethylenediphenyldiamine there can be no doubt that this compound is an isomeric *tetranitro*-derivative.

An attempt was next made to prepare a dinitro-derivative. In the

first experiment, the base was dissolved in cold concentrated nitric acid, and when the reaction was complete the resulting liquid was thrown into cold water. An orange powder was precipitated, which melted sharply at 191—192°. On analysis:

0·1723 gave 26·6 c.c. moist nitrogen at 16° and 750 mm. N = 17·9.
$C_{18}H_{21}O_6N_5$ requires N = 17·37 per cent.

This substance, therefore, may be a *trinitrodixylylethylenediamine.*

In a second experiment, an alcoholic solution of the base was heated to boiling with concentrated nitric acid. The solution was thrown into an excess of water, when brownish-yellow crystals separated which melted at 152—154°. On analysis:

0·1598 gave 18·3 c.c. moist nitrogen at 13° and 767 mm. N = 13·43.
$C_{18}H_{23}O_2N_3$ requires N = 13·41 per cent.

The dinitro-compound sought was not obtained, as the derivative just described has a composition corresponding to that of a *mononitrodixylylethylenediamine*, $C_6H_3Me_2\cdot NH\cdot C_2H_4\cdot NH\cdot C_6H_2Me_2\cdot NO_2$.

Dixylylpiperazine, $C_6H_3Me_2\cdot N{:}(C_2H_4)_2{:}N\cdot C_6H_3Me_2$.

This base was produced by using no alkali, but a larger proportion of ethylene dibromide, than in the preparation of the diamine. The reaction is more violent, and it is necessary to add the dibromide carefully in small quantities. Gentle warming is required to start the reaction, which is completed by heating for 2 hours in an oil-bath at 150°. The piperazine, after repeated recrystallisation from absolute alcohol, was obtained in shining, white leaflets which melted at 151°. On analysis:

0·2374 gave 0·7113 CO_2 and 0·1997 H_2O. C = 81·72; H = 9·34.
0·2802 „ 0·8401 CO_2 „ 0·2335 H_2O. C = 81·77; H = 9·25.
$C_{20}H_{26}N_2$ requires C = 81·63; H = 8·84 per cent.

Di-ψ-cumylethylenediamine, $C_2H_4(NH\cdot C_6H_2Me_3)_2$.

The ψ-cumidine employed melted at 67°. The proportion of base to ethylene dibromide, and the method followed generally, were the same as described for the homologous xylyl compound, save that the recrystallisation was effected from benzene. A variation of this method, in which no sodium carbonate was used, but the mass, after washing with rectified spirit, was treated with potassium hydroxide solution before recrystallisation from benzene, gave a good yield. The diamine recrystallised twice from benzene was obtained in the form of brilliant, colourless needles melting at 168°. These dissolve

readily in benzene, but only slightly in hot alcohol or ether. On analysis :

0·2550 gave 0·7556 CO_2 and 0·2190 H_2O. C = 80·81 ; H = 9·52.
$C_{20}H_{28}N_2$ requires C = 81·08 ; H = 9·45 per cent.

Di-ψ-cumylethylenediamine Nitrate, $C_2H_4(NH\cdot C_6H_2Me_3)_2,2HNO_3$, was obtained in the same manner as described above for the corresponding xylyl salt. It consists of colourless needles melting at 154°. On analysis :

0·2074 gave 22·4 c.c. moist nitrogen at 17° and 755 mm. N = 12·5.
$C_{20}H_{30}O_6N_4$ requires N = 13·2 per cent.

Di-ψ-cumylethylenediamine Platinichloride,
$C_2H_4(NH\cdot C_6H_2Me_3)_2,H_2PtCl_6$,
was prepared as in the case of the corresponding xylyl compound, and precipitated as a buff-coloured powder. On analysis :

0·3451 gave 0·0939 Pt. Pt = 27·49.
$C_{20}H_{28}N_2,H_2PtCl_6$ requires Pt = 27·64 per cent.

Di-ψ-cumylethylenediamine Mercurichloride,
$C_2H_4(NH\cdot C_6H_2Me_3)_2,HgCl_2$,
corresponds in method of preparation to its xylyl homologue. The crystals were a little darker in colour and melted at 150°. The analysis also gave a lower percentage of mercury than that calculated from the formula. Found Hg = 33·2 ; required Hg = 35·2 per cent.

Dinitrodi-ψ-cumylethylenediamine, $C_2H_4(NH\cdot C_6HMe_3\cdot NO_2)_2$.—It is remarkable that, working in exactly the same manner as for the preparation of the tetranitrodixylylethylenediamine, we obtained with the cumyl base, not a tetranitro-, but a dinitro-derivative. The product melted at 97—98°, and was precipitated as a pale yellow powder. On analysis :

0·1694 gave 20·5 c.c. moist nitrogen at 16° and 753·5 mm. N = 14·0.
$C_{20}H_{26}O_4N_4$ requires N = 14·5 per cent.

An *isomeride* obtained by dissolving the base in concentrated nitric acid with application of heat, gave, on throwing the liquid into water, a compound melting at 49—50°. On analysis :

0·2069 gave 26 c.c. moist nitrogen at 18° and 769·6 mm. N = 14·43.
$C_{20}H_{26}O_4N_4$ requires N = 14·5 per cent.

Di-ψ-cumylpiperazine, $C_6H_2Me_3\cdot N{:}(C_2H_4)_2{:}N\cdot C_6H_2Me_3$.

ψ-Cumidine (2 mols.) was mixed with ethylene dibromide (1 mol.), and heated in a closed tube at 200° for 3 hours. The contents were treated with boiling water and the residue dissolved in

hot rectified spirit; from the solution, on cooling, crystals were deposited which melted at 148—150°. Recrystallisation from ether gave large, brilliant needles which had the same melting point. They were readily soluble in chloroform, but less so in light petroleum. On analysis:

0·2338 gave 0·6984 CO_2 and 0·1954 H_2O. C = 81·4; H = 9·28.
$C_{22}H_{30}N_2$ requires C = 81·91. H = 9·25 per cent.

We desire to express our indebtedness to Mr. Thomas Walsh, B.A., for assistance during the course of these experiments.

QUEEN'S COLLEGE,
GALWAY.

XXIII.—*The Action of Phenylcarbimide on Diphenyl-, Dialphyl-, and Dinaphthyl-diamines.*

By ALFRED SENIER and WILLIAM GOODWIN.

WHEN the two ethylenediamines described in the previous paper are treated with phenylcarbimide, an interesting reaction, resulting in the formation of ethylenediamines of the type $C_2H_4(NR'\cdot CO\cdot NHPh)_2$, is brought to light. Combination is effected between each of the alphyl amino-groups of the diamine and the carbonyl groups of the carbimide by the severance of the double linking between the carbon and nitrogen of the latter. The reaction is of the same type as that between ethylenediamine hydrochloride and silver carbimide, whereby ethylenediurea, $C_2H_4(NH\cdot CO\cdot NH_2)_2$, was obtained by Volhard (*Annalen*, 1861, **119**, 349), and is analogous to the general reaction between phenylcarbimide and primary and secondary amines. The compounds are also homologous with the trimethylenecarbanilide of Hanssen, $C_3H_6(NH\cdot CO\cdot NHPh)_2$ (*Ber.*, 1887, **20**, 783). The latter experimenter did, indeed, by a different reaction, that between ethylenedicarbanilic chloride and aniline, produce a compound which was doubtless an impure specimen of the dicarbanilidodiphenylethylenediamine described below, but it melted at 170° and resisted all attempts at purification.

We have succeeded in extending this reaction to diphenyl- and several dialphyl-diamines, and its general character is further proved by its application to the naphthyl group. In the latter case, however, unsymmetrical or mono-ureas have so far only been obtained.

Dicarbanilidodiphenylethylenediamine (*Ethylenedicarbanilide*), $C_2H_4(NPh\cdot CO\cdot NHPh)_2$.

Diphenylethylenediamine (1 mol.), carefully dried by standing over sulphuric acid in a vacuum, was heated in a closed tube with phenylcarbimide (2 mols.) at 120—130° for 3 hours. The product, of a steel grey colour, was washed with ether and crystallised from absolute alcohol. The crystals thus obtained were, however, still impure, and needed to be recrystallised several times from benzene, and finally from absolute alcohol. They consist of pale, bluish-grey needles which melt at 220°. On analysis:

0·2371 gave 0·6512 CO_2 and 0·1306 H_2O. C = 74·9; H = 6·12.
$C_{28}H_{26}O_2N_4$ requires C = 74·66; H = 5·77 per cent.

Dicarbanilidoditolylethylenediamines, $C_2H_4[N(C_6H_4Me)\cdot CO\cdot NHPh]_2$.

The ditolylethylenediamines (1 mol.) were heated in closed tubes with phenylcarbimide (2 mols.) in the manner above described, except that, in the case of the para-derivative, a somewhat higher temperature, 150°, gave the best yield. In the preparation of the ditolylethylenediamines employed, the method described by Mills (Trans., 1900, 77, 1020) was followed in the case of the ortho-derivative, that of Francis (Trans., 1897, 71, 426) for the meta-, and of Gretillat (*Monit. Scient.*, 1873, [iii], 3, 383) for the para-compound.

Dicarbanilidodi-o-tolylethylenediamine appeared on opening the tube as a mass of pink crystals which, after being washed with ether and recrystallised from absolute alcohol, retained a faint pink colour. It melted at 195—196°. On analysis:

0·2765 gave 0·7591 CO_2 and 0·1654 H_2O. C = 74·87; H = 6·6.
$C_{30}H_{30}O_2N_4$ requires C = 75·31; H = 6·27 per cent.

*Dicarbanilidodi-*m*-tolylethylenediamine* crystallised in the form of brilliant, colourless needles melting at 181·5°. On analysis:

0·3047 gave 0·8402 CO_2 and 0·1788 H_2O. C = 75·2; H = 6·52.
$C_{30}H_{30}O_2N_4$ requires C = 75·31; H = 6·27 per cent.

*Dicarbanilidodi-*p*-tolylethylenediamine* was purified in the manner described for the ortho-derivative, except that after washing the tube contents with ether, the residue was recrystallised several times from benzene before the final recrystallisation from absolute alcohol. It separated in the form of fine, colourless needles which melted at 186°. On analysis:

0·2990 gave 0·8226 CO_2 and 0·1766 H_2O. C = 75·03; H = 6·58.
$C_{30}H_{30}O_2N_4$ requires C = 75·31; H = 6·27 per cent.

Dicarbanilidodixylylethylenediamine, $C_2H_4[N(C_6H_3Me_2)\cdot CO\cdot NHPh]_2$.

Dixylylethylenediamine (this vol., p. 254) was heated in a closed tube with phenylcarbimide for 3 hours at 135—140°. The proportion used was one molecule of the base to two of the carbimide. The semi-crystalline mass which resulted was washed with a small quantity of rectified spirit, and the residue was recrystallised several times from absolute alcohol. Well formed, colourless needles melting sharply at 167° were finally obtained. On analysis :

0·3037 gave 0·8453 CO_2 and 0·1912 H_2O. C = 75·9 ; H = 6·99.
$C_{32}H_{34}O_2N_4$ requires C = 75·88 ; H = 6·72 per cent.

Dicarbanilidodi-ψ-cumylethylenediamine,
$C_2H_4[N(C_6H_2Me_3)\cdot CO\cdot NHPh]_2$.

Di-ψ-cumylethylenediamine (this vol., p. 256) and phenylcarbimide, in the proportion of one molecule to two, were heated in a closed tube for 4 hours at 180—190°. The contents were well washed with ether and recrystallised several times from alcohol. To obtain the compound in a pure condition, it was, however, necessary to recrystallise again several times from benzene, and finally from ether, in which latter solvent it is only slightly soluble. It consists of glistening, colourless needles which melt at 191°. On analysis :

0·1615 gave 0·4532 CO_2 and 0·1108 H_2O. C = 76·53 ; H = 7·62.
$C_{34}H_{38}O_2N_4$ requires C = 76·4 ; H = 7·11 per cent.

Monocarbanilidodi-α-naphthylethylenediamine,
$C_{10}H_7\cdot NH\cdot C_2H_4\cdot N(C_{10}H_7)\cdot CO\cdot NHPh$.

The ethylenedi-α-naphthyldiamine was prepared according to the directions of Bischoff and Nastvogel (*Ber.*, 1890, **23**, 2039), and melted at 126°. It was carefully dried and heated for 5 hours with phenylcarbimide in the proportion of one molecule to two molecules. The tube contents were washed with small quantities of ether and crystallised twice from benzene. As the melting point was still not definite, further recrystallisation from chloroform was resorted to, and after twice treating in this way, small, colourless needles melting at 266° were obtained. The crystals are readily soluble in benzene, less so in chloroform, and dissolved only sparingly in alcohol or ether. On analysis :

0·2534 gave 0·7530 CO_2 and 0·1486 H_2O. C = 81·04 ; H = 6·51.
$C_{29}H_{25}ON_3$ requires C = 80·74 ; H = 5·80 per cent.
$C_{36}H_{30}O_2N_4$ „ C = 78·54 ; H = 5·45 „

The analysis proves the compound formed to be a monocarbanilido-derivative, thus differing from the phenyl- and alphyl-derivatives described above. Several attempts were made, using larger proportions of phenylcarbimide and varying the temperature, but in each instance only the monocarbanilido-derivative was produced.

QUEEN'S COLLEGE,
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XXIV.—*Note on the use of Pyridine for Molecular Weight Determinations by the Ebullioscopic Method.*

By WILLIAM ROSS INNES, M.Sc., Ph.D.

PYRIDINE has a very remarkable solvent power for both organic and inorganic compounds; many substances which are insoluble, or only sparingly soluble in the organic solvents in general use, dissolve readily in pyridine.

An organic liquid in which so many substances are soluble should be very valuable in the investigation of the physical properties of solutions, as a large number of comparable results can be obtained. For such a purpose, it is important to know whether the molecular weights of dissolved substances are normal in this solvent.

As is well known, substances containing hydroxyl groups generally give abnormally high molecular weights both by the freezing and boiling point methods, when hydrocarbons such as benzene, naphthalene, and phenanthrene are used as solvents. The molecular weight is found to increase with the concentration, and is usually nearly normal in dilute solution.

Von Laszczynski and von Gorski (*Zeit. Elektrochem.*, 1897, 4, 299) have shown that pyridine solutions of a number of inorganic salts have marked electrical conductivity, and deduce from this that the salts are ionised to a considerable extent. If this is the case, pyridine should give normal molecular weights with organic hydroxy-compounds, as an ionising solvent does not favour the formation of polymerised molecules.

Werner (*Zeit. anorg. Chem.*, 1897, 15, 1) has determined the molecular weight of a number of inorganic salts in pyridine. The concentrations used were small (about 0·5 to 3 per cent.). The molecular weights found were constant within the limits of experimental error for the various concentrations and agreed closely with those calculated from the formulæ, in some cases being a few units above, in others slightly below the normal. The only substances which gave values much

below the normal were mercuric iodide and cyanide. Both these substances are ionised to an unusually small extent in aqueous solution.

There is therefore no evidence of ionisation in pyridine to be drawn from the molecular weights of dissolved salts.* Consequently there was a possibility that pyridine might give abnormal results with organic hydroxy-compounds.

As the author wished to examine in a polymerising solvent, substances which are soluble in pyridine, but insoluble in all the solvents known to have this action, the following determinations were carried out to test this point.

The method described by Jones (*Zeit. physikal. Chem.*, 1899, **31**, 114) was tried; the boiling tube was somewhat smaller than that used by him, but otherwise the apparatus was the same.

The boiling point of the pyridine was not of satisfactory constancy. It varied considerably with changes in the gas pressure, and draughts affected it very much. This may, no doubt, be ascribed to the direct manner of heating recommended by Jones, and to the absence of a vapour jacket.

A determination of the constancy of the boiling point was therefore made in an ordinary Beckmann apparatus, using a platinum cylinder in the way described by Jones. The result was very satisfactory.

A glass vapour mantle was used, and a plain glass boiling tube without a platinum rod fused into the bottom.

It was found that pyridine acted rapidly on cork, leaving a shrivelled, hard, wood-like residue; the condenser tube was therefore fused directly to the boiling tube and the boiling tube made longer than usual above the condenser. The cork holding the thermometer was covered with tinfoil. Hardly any pyridine vapour came into contact with it, owing to the length of the tube.

The platinum cylinder was 7·5 cm. long, 1·9 cm. in diameter, and made conical at the top so as to fit the thermometer closely.

The boiling tube was filled to a height of about 2·5 cm. with glass beads of the usual size, the platinum cylinder slipped down, and very fine beads poured in to occupy about 1 cm. The cylinder was then brought into the middle of the tube by tapping, and some pieces of platinum foil placed in it. The small beads hold the cylinder more firmly than the large ones, and mix the vapour and liquid more thoroughly.

* Jones has suggested (*Zeit. physikal. Chem.*, 1899, **31**, 114) that the apparent absence of ionisation indicated by osmotic methods in this and similar cases may perhaps be accounted for by combination of the dissolved substance with the solvent. It is evident, however, that combination with the solvent should lower, not raise, the apparent molecular weight. The number of molecules of dissolved substance would be the same, but the amount of solvent would be smaller than that used in the calculation.

The pyridine used was Kahlbaum's "gereinigt"; it was dried over solid potassium hydroxide and fractionated, a dephlegmating column being used. The fraction boiling at 115·2—115·5° was taken for the experiments.

Two series of determinations were made with Kahlbaum's "pure" pyridine; the constant obtained agreed perfectly with that given by the much cheaper specimen.

A Jena glass Beckmann thermometer with a very small bulb was employed. A constant temperature was only obtained after the liquid had been boiling for several hours.

The following readings show the apparent variation of the boiling point due to changes in the thermometer:

Liquid began to boil at 11·30.

Time.	Reading.	Time.	Reading.
11·45	2·45	3·25	2·990
12·15	2·59	3·40	2·990
12·30	2·740	4·0	3·060
2·10	2·835	4·25	3·070
3·0	2·885	4·35	3·070
3·7	2·940		

By leaving the liquid boiling all night, a boiling point of satisfactory constancy was obtained.

Time.	Reading.	Time.	Reading.
5·10 P.M.	3·130	10·50 A.M	3·272
6·10 ,,	3·148	1·5 P.M.	3·270
10·20 A.M.	3·278		

During both these determinations the atmospheric pressure varied very little.

In the experiments, of which the results are given, the pyridine was left boiling all night, the boiling point observed several times during an hour in the morning, and if it did not vary more than 0·01° the determinations were then carried out. A regulator was used to keep the gas pressure constant.

In calculating the results, 0·2 gram is deducted from the weight of solvent actually taken.

Rosenheim and Woge (*Zeit. anorg. Chem.*, 1897, **15**, 315) used pyridine to determine the molecular weight of beryllium chloride. They state that, with ordinary German glass, constant results could not be obtained, as the pyridine attacked the glass. They found it necessary to use Jena glass. No effect of this sort had been noticed in my experiments.

Twenty grams of pyridine were heated for sixteen hours in the

boiling tube, fitted up as if for a molecular weight determination. The pyridine was then evaporated to dryness in a weighed platinum dish. There was no residue, and the weight of the dish was the same to four places of decimals.

Determination of the molecular rise of boiling point for pyridine:

Wt. of solvent.	Wt. of subst.	Rise of b. p.	Grams subst. per 100 g. solvent.	Mols./100 per 100 g. solvent.	Constant.
		Benzophenone, $C_{13}H_{10}O = 182$.			
15·72	0·2480	0·268°	1·60	0·88	30·5
,,	0·5970	0·648	3·85	2·12	30·7
,,	0·926	0·988	5·97	3·28	30·1
,,	1·259	1·318	8·12	4·46	29·6
		Phenanthrene, $C_{14}H_{10} = 178$.			
18·59	0·1592	0·140°	0·87	0·49	28·8
,,	0·4236	0·392	2·30	1·29	30·3
,,	0·8406	0·740	4·57	2·57	28·8
,,	1·450	1·240	7·88	4·43	28·0
,,	2·063	1·758	11·21	6·30	27·9
		Diphenylamine, $C_{12}H_{11}N = 169$.			
18·40	0·2282	0·218°	1·23	0·73	29·0
,,	0·5278	0·536	2·84	1·68	30·9
,,	1·7008	1·596	9·34	5·53	28·5

The mean of all the determinations is 29·5.

The constant has been determined by Werner (*loc. cit.*) with diphenylamine in concentrations varying from 0·93 to 9·69 per cent. The mean value was 30·1, the numbers varying from 28·6 to 31·5.

The constant has also been determined by Rosenheim and Woge (*loc. cit.*), who used diphenyl, triphenylmethane, and *p*-toluidine as dissolved substances in concentrations of from 1·7 to 3·7 per cent. The mean was 30·7. The numbers obtained for the constant were very concordant, the greatest difference being only 1·3, but the determinations were nearly all carried out at about the same concentration, and the greatest differences of concentration were small.

Werner calculated the constant from the Trouton-Schiff rule $C = 0{\cdot}00096\,Tm = 29{\cdot}5$ This method only gives an approximate value in most cases. The constant may be calculated with considerable

accuracy by van't Hoff's formula $C=\frac{0{\cdot}0198T^2}{L}$, which has been shown to apply to the boiling point by Arrhenius (*Zeit. physikal. Chem.*, 1889, **4**, 550).

The heat of vaporisation of pyridine has been determined by Louguinine (*Compt. rend.*, 1899, **128**, 366), who found it to be 101·39 at 115·5°. Introducing these values, we get

$$C=\frac{0{\cdot}0198\times(388{\cdot}5)^2}{101{\cdot}39}=29{\cdot}47\ ;$$

29·5 is therefore taken as the constant for pyridine.

Molecular weight of hydroxy-compounds in pyridine:

Wt. of solvent.	Wt. of subst.	Rise of b. p.	Grams subst. per 100 g. solvent.	Mols./100 per 100 g. solvent.	Mol. wt.
		Succinic acid, $C_2H_4(CO_2H)_2=118$.			
17·77	0·2104	0·278°	1·18	1·00	127
,,	0·4316	0·575	2·43	2·06	126
,,	0·8524	1·215	4·80	4·06	117
,,	1·492	2·205	8·40	7·11	113
		Tartaric acid, $C_2H_2(OH)_2(CO_2H)_2=150$.			
19·60	0·3542	0·335°	1·81	1·20	160
,,	1·1530	1·065	5·88	3·92	164
,,	2·372	2·175	12·10	8·07	165
		Salicylic acid, $C_6H_4(OH)\cdot CO_2H=138$.			
18·26	0·1782	0·188°	0·98	0·71	123
,,	0·5021	0·615	2·75	1·99	133
,,	1·1978	1·390	6·56	4·75	140
,,	2·193	2·630	12·00	8·70	136
		Resorcinol, $C_6H_4(OH)_2=110$.			
16·89	0·0968	0·145°	0·57	0·53	124
,,	0·3050	0·497	1·80	1·64	107
,,	0·6968	1·153	4·17	3·99	105
		Tartaric ditoluidide, $C_2H_2(OH)_2(CO\cdot NH\cdot C_6H_4\cdot CH_3)_2=328$.			
16·99	0·2094	0·110°	1·23	0·38	331
,,	0·4112	0·218	2·42	0·74	330
,,	0·6234	0·308	3·67	1·12	354

β-Naphthol, $C_{10}H_7 \cdot OH = 144$.

18·54	0·1734	0·176°	0·93	0·65	158
,,	0·4284	0·465	2·31	1·60	148
,,	0·9694	1·060	5·23	3·63	147
,,	1·342	1·470	7·22	5·01	146
,,	1·798	2·000	9·68	6·72	144

The molecular weights found are in every case near the normal, and there is no regular increase with concentration. Pyridine may therefore be used to find the normal molecular weight of hydroxy-compounds.

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accuracy by van't Hoff's formula $C=\frac{0{\cdot}0198T^2}{L}$, which has been shown to apply to the boiling point by Arrhenius (*Zeit. physikal. Chem.*, 1889, **4**, 550).

The heat of vaporisation of pyridine has been determined by Louguinine (*Compt. rend.*, 1899, **128**, 366), who found it to be 101·39 at 115·5°. Introducing these values, we get

$$C=\frac{0{\cdot}0198\times(388{\cdot}5)^2}{101{\cdot}39}=29{\cdot}47;$$

29·5 is therefore taken as the constant for pyridine.

Molecular weight of hydroxy-compounds in pyridine:

Wt. of solvent.	Wt. of subst.	Rise of b. p.	Grams subst. per 100 g. solvent.	Mols./100 per 100 g. solvent.	Mol. wt.
Succinic acid, $C_2H_4(CO_2H)_2=118$.					
17·77	0·2104	0·278°	1·18	1·00	127
,,	0·4316	0·575	2·43	2·06	126
,,	0·8524	1·215	4·80	4·06	117
,,	1·492	2·205	8·40	7·11	113
Tartaric acid, $C_2H_2(OH)_2(CO_2H)_2=150$.					
19·60	0·3542	0·335°	1·81	1·20	160
,,	1·1530	1·065	5·88	3·92	164
,,	2·372	2·175	12·10	8·07	165
Salicylic acid, $C_6H_4(OH)\cdot CO_2H=138$.					
18·26	0·1782	0·188°	0·98	0·71	123
,,	0·5021	0·615	2·75	1·99	133
,,	1·1978	1·390	6·56	4·75	140
,,	2·193	2·630	12·00	8·70	136
Resorcinol, $C_6H_4(OH)_2=110$.					
16·89	0·0968	0·145°	0·57	0·53	124
,,	0·3050	0·497	1·80	1·64	107
,,	0·6968	1·153	4·17	3·99	105
Tartaric ditoluidide, $C_2H_2(OH)_2(CO\cdot NH\cdot C_6H_4\cdot CH_3)_2=328$.					
16·99	0·2094	0·110°	1·23	0·38	331
,,	0·4112	0·218	2·42	0·74	330
,,	0·6234	0·308	3·67	1·12	354

β-Naphthol, $C_{10}H_7 \cdot OH = 144$.

Wt. of solvent.	Wt. of subst.	Rise of b. p.	Grams subst. per 100 g. solvent.	Mols./100 per 100 g. solvent.	Mol. wt.
18·54	0·1734	0·176°	0·93	0·65	158
,,	0·4284	0·465	2·31	1·60	148
,,	0·9694	1·060	5·23	3·63	147
,,	1·342	1·470	7·22	5·01	146
,,	1·798	2·000	9·68	6·72	144

The molecular weights found are in every case near the normal, and there is no regular increase with concentration. Pyridine may therefore be used to find the normal molecular weight of hydroxy-compounds.

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XXV.—*The Amide, Anilide, and* o- *and* p-*Toluidides of Glyceric Acid.*

By PERCY FARADAY FRANKLAND, FREDERICK MALCOLM WHARTON, and HENRY ASTON.

IN pursuing the systematic study of the effect on rotatory power produced by substitution in optically active compounds, we have recently been directing our attention to active amides and their substitution products.

The information at present available concerning the rotatory power of compounds of this class is summarised in the following table. In this table only such amides have been included as are derived from acids of which the rotatory power of several esters is also known, and the rotations of these esters are also given so that the relative rotatory effects of the amino- and alkyloxy-groups are rendered apparent. It will be seen that the existing material for such comparison is very scanty, being practically limited to the derivatives of malic, tartaric, and mandelic acids.

Mandelic acid (Walden, *Zeit. physikal. Chem.*, 1895, **17**, 706).

		c.	$[\alpha]_D^{22°}$.	$[M]_D$.
Free acid	Acetone.....	2·50	−148·0°	−225·0°
Methyl ester	,,	3·33	−110·2	−182·9
Ethyl ,,	,,	5·81	−90·6	−163·1
,, ,,	,,	1·16	−87·1	−156·8
Amide	,,	2·50	−66·6	−100·6
,,	,,	1·50	−66·7	−100·7

Malic acid (Walden, *ibid.*, 248).

		c.	$[\alpha]_D^{20°}$.	$[M]_D$.
Dimethyl ester	Liquid	—	−6·85°	−11·1°
Diethyl „	„	—	−10·18	−19·3
Dipropyl „	„	—	−11·62	−25·3
Di*iso*propyl „	„	—	−10·41	−22·7
Di*iso*butyl „	„	—	−11·14	−27·4
Diamide	Water	4·32	−37·6	−49·6
„	„	8·65	−38·0	−50·2
Dianilide	Glacial acetic acid	1·50	−60·66	−172·3
„	„	0·75	−58·66	−166·6
Di-*o*-toluidide	„	2·00	−65·0	−202·8
„	„	1·00	−66·5	−207·5
Di-*p*-toluidide	„	1·00	$[\alpha]_D^{20}$ −70·0	−218·4
β-Naphthimide	„	1·00	$[\alpha]_D^{20}$ −51·5	−124·1
Anil*	Water	0·2258	$[\alpha]_D$ −33·95	−59·4

d-*Tartaric acid.*

		c.	$[\alpha]_D^{20°}$.	$[M]_D$.
Dimethyl ester	Liquid	—	+2·14°	+3·8°
Diethyl „	„	—	+7·66	+15·8
Dipropyl „	„	—	+12·44	+29·1
Di*iso*propyl „	„	—	+14·89	+34·8
Diamide	Water	—	$[\alpha]_j$ +133·9	$[M]_j$ +198·2
			$[\alpha]_D$.	$[M]_D$.
Methyltartrimide†	Water	7·31	+194·2	+281·6
„	„	12·94	+192·6	+279·3
Ethyltartrimide†	„	5·76	+164·9	+262·2
„	„	8·57	+166·2	+264·3

A glance at the table is sufficient to show that the rotatory effect of the NH_2 group is qualitatively similar to that of the alkyloxy-(OA) group, but quantitatively greater. Thus, in the case of mandelic acid, the replacement of OH by OA has the effect of diminishing the lævorotation (the ethoxy- having a greater effect in this respect than the methoxy-group), the replacement by NH_2 leading to a still greater depression of the latter.

In the case of malic acid, the alkyloxy-groups successively raise the

* Bischoff and Walden, *Stereochemie*, 855.

† Ladenburg, *Ber.*, 1896, **29**, 2710.

lævorotation, the latter being very greatly further elevated by the replacement of OA by NH_2.

Again, in the case of *d*-tartaric acid, the effect is exactly similar, only that here it is the dextrorotation which is raised by these substitutions.

On substituting the hydrogen in the amino-group by phenyl or tolyl, it is seen that the rotatory effect of the group is still further increased. Again, if the amino-group becomes an imino-group leading to the formation of a ring compound, the rotatory effect is also increased, as in the cases of malic *β*-naphthimide and of methyl and ethyl tartrimides.

The present paper deals with the preparation and properties of the amide, anilide, *o*-toluidide, and *p*-toluidide of glyceric acid. With the exception of the *o*-toluidide, these compounds have had their rotation determined in the liquid state, whilst the rotation of all of them has also been taken in methyl alcohol solution. So far as we are aware, these are the only amides which have hitherto had their rotation determined in the fused or liquid condition.

The rotations of these new compounds should be compared with those of the esters of *d*-glyceric acid given below (P. Frankland and Price, Trans., 1897, 71, 270):

	$[\alpha]_D^{15°}$	$[M]_D^{15°}$
Methyl glycerate.....	−4·80°	−5·76°
Ethyl „	−9·18	−12·30
Propyl „	−12·94	−19·15
*iso*Propyl „	−11·82	−17·49
Butyl „	−13·19	−21·37
*iso*Butyl „	−14·23	−23·05
Amyl „	−14·12	−24·85
Heptyl „	−11·30	−23·05
Octyl „	−10·22	−22·28

The rotation of glycerylamide is much greater, $[M]_D^{100°} = -41·98°$, of glycerylanilide still greater, $[M]_D^{100°} = -72·36°$, whilst that of glyceryl-*p*-toluidide is intermediate between that of the two latter, $[M]_D^{98°} = -67·65°$. The lævorotation of the *o*-toluidide in the fused state is doubtless lower than that of the para-compound, as in methyl alcohol solution it is very much lower than that of the latter; indeed, it is about the same as that of glycerylamide in the same solvent at the same concentration.

The lævorotation of the amide, anilide, and *p*-toluidide is very considerably greater in methyl alcohol solution than in the liquid state; the *o*-toluidide, as already mentioned, could only be optically examined in solution, but it may safely be assumed that its rotation is similarly affected by this solvent.

It is further noteworthy that the rotation of the amide, anilide, and *p*-toluidide in each case diminishes with rise of temperature; in methyl alcohol solution, increase of concentration diminishes the rotation of the amide and anilide, whilst it increases that of the *o*-toluidide. The rotation of the *p*-toluidide is almost independent of the concentration within the limits examined, there being, however, a very slight diminution with increase of concentration.

The corresponding compounds of inactive glyceric acid were also prepared, and their melting points compared with those of the active substances:

	Melting point.	
	Active.	Inactive.
Glycerylamide.....	99·5—100°	91·5— 92°
Glycerylanilide	113 —113·5	91
Glyceryl-*o*-toluidide...	89 — 89·5	129 —129·5
Glyceryl-*p*-toluidide ..	131 —131·5	120 —120·5

Thus, in all cases, excepting that of the *o*-toluidide, the melting point of the active is higher than that of the corresponding inactive compound.

We are continuing the investigation of the effect produced by these and similar substitutions.

Experimental.

I. *Glycerylamide (Inactive).*

Dry ammonia was passed into inactive ethyl glycerate surrounded with a freezing mixture of ice and salt. The saturated liquid was allowed to stand for 24 hours, the excess of ammonia and alcohol being then taken off under reduced pressure at the ordinary temperature of the air. When nearly the whole of the ammonia had been removed, the residue crystallised out. It was recrystallised from methyl alcohol; the prismatic crystals melt at 91·5—92°.

0·0411 gave 0·0054 nitrogen. N = 13·14.

$C_3H_7O_3N$ requires N = 13·33 per cent.

Glycerylamide (Active).

This was prepared in exactly the same way from active ethyl glycerate.* It forms large plates or prisms melting at 99·5—100°.

0·0402 gave 0·0052545 nitrogen. N = 13·07.

0·0409 „ 0·005397 „ N = 13·20.

$C_3H_7O_3N$ requires N = 13·33 per cent.

d 130°/4° = 1·3099. *d* 140°/4° = 1·3016. *d* 150°/4° = 1·2932.

* $a_D = -11·35°$; $l = 1$.

Rotation of glycerylamide.

Temp.	Length of tube.	$d\ t°/4°$.	α_D.	$[\alpha]_D$.	[M
100°	44 mm.	1·3347	−23·47°	−39·98°	−41·98°
109·5	„	1·3268	−23·06	−39·50	−41·48
136	„	1·3048	−21·88	−38·11	−40·02
182	„	1·2666	−19·91	−35·73*	−37·52
[20° calculated from rotations at 100° and 136° above				−44·14	−46·35]

II. *Glycerylanilide (Inactive).*

Ten grams of inactive ethyl glycerate were heated with 8 grams of aniline (7 grams is the theoretical quantity required) for 4 hours at 140°. The temperature was then gradually raised to 160° and maintained there for 4 hours more. On cooling, the mixture solidified to a brown, pasty mass. The colour was removed by boiling in alcoholic solution with animal charcoal, and crystallisation was then effected from chloroform, small plates melting at 91° being obtained.

0·1745 gave 12·2 c.c. moist nitrogen at 12° and 729 mm. N = 7·95.
0·1584 „ 11·0 c.c. „ „ 12·5 „ 725·5 mm. N = 7·85.
$C_9H_{11}O_3N$ requires N = 7·73 per cent.

Glycerylanilide (Active).

This substance was prepared from active ethyl glycerate as described above for the inactive compound. It was first crystallised from alcohol, being obtained in long, flat blades. On subsequently crystallising from chloroform, in which it is but slightly soluble, it was obtained in small needles. On melting, these yielded a dark liquid, which could not be satisfactorily examined in the polarimeter; it was therefore boiled with animal charcoal in alcoholic solution, and finally crystallised from this solvent. The crystals melted at 113—113·5°, and yielded a clear and colourless liquid.

0·2288 gave 15·6 c.c. moist nitrogen at 14° and 736 mm. N = 7·77.
0·1993 „ 13·2 c.c. „ „ 12° „ 751·4 mm. N = 7·77.
$C_9H_{11}O_3N$ requires N = 7·73 per cent.

d 120°/4° = 1·1914. d 140°/4° = 1·1744.

* This value is somewhat doubtful, as the glycerylamide underwent partial decomposition during the polarimetric measurements at this temperature.

Rotation of glycerylanilide.

Temp.	Length of tube	$d\ t°/4°$.	α_D.	$[\alpha]_D$.	$[M]_D$
100°	49·85 mm.	1·2084	−24·09°	−39·98°	−72·36°
109	,,	1·2008	−23·42	−39·12	−70·81
139	,,	1·1752	−21·19	−36·16	−65·45
180	,,	1·1404	−18·15	−31·93	−57·79
[20° calculated from rotations at 100° and 139° above.				−47·82	−86·55]

III. *Glyceryl-o-toluidide* (*Inactive*).

Ten grams of inactive methyl glycerate were heated with 15 grams of *o*-toluidine for 4 hours at 140°, the temperature being then raised slowly to 160°; finally the excess of toluidine was distilled off under 14 mm. pressure. On cooling, the contents of the flask nearly solidified to a dark brown mass. On crystallising from benzene, the substance was still much coloured, and it was therefore boiled with animal charcoal in alcoholic solution. It was then several times recrystallised from benzene until of constant melting point, and finally from chloroform by which the melting point was not altered. The crystals are colourless, have a somewhat silky appearance, and melt at 129—129·5°. The liquid obtained by melting the crystals does not colour in contact with air, and in this respect differs from the active compound (see below).

0·2000 gave 0·4499 CO_2 and 0·1219 H_2O. C = 61·35; H = 6·77.
0·1536 ,, 9·4 c.c. moist nitrogen at 14·5° and 757·4 mm. N = 7·15.
$C_{10}H_{13}O_3N$ requires C = 61·54; H = 6·66; N = 7·18 per cent.

Glyceryl-o-toluidide (*Active*).

This was prepared similarly to the inactive substance, 15 grams of active methyl glycerate * being heated with 22·5 grams of *o*-toluidine. Although the colour of the product was removed by boiling in alcoholic solution with animal charcoal, it reappeared during the exposure to air necessitated by the subsequent filtration. Thus pink crystals were obtained from benzene, but finally an almost perfectly colourless separation was obtained by using chloroform as the solvent and washing the crystals with ice-cold chloroform. The crystals had a constant melting point of 89—89·5°. On melting these crystals, however, the liquid obtained was of such a deep-red colour, when viewed by transmitted light, that it could not be used for polarimetric observation. The rotation could therefore only be determined in solution, and this

* $\alpha_D = -6·20°$; $l = 1$.

necessitated determining the rotatory power of all the other substances referred to in this paper in solution also. The values for the rotatory powers in solution are given later (see p. 273).

0·2002 gave 0·4509 CO_2 and 0·1213 H_2O. C = 61·42; H = 6·73.
0·2004 „ 0·4515 CO_2 „ 0·1219 H_2O. C = 61·44; H = 6·75.
0·2030 „ 12·6 c.c. moist nitrogen at 12° and 746·4 mm. N = 7·23.
$C_{10}H_{13}O_3N$ requires C = 61·54; H = 6·66; N = 7·18 per cent.

IV. *Glyceryl*-p-*toluidide* (*Inactive*).

This was prepared from inactive ethyl glycerate and *p*-toluidine (m. p. 44·5°). After heating together as described in the case of the *o*-toluidide, the mixture became semi-solid on cooling. The brown mass was treated with benzene to extract the excess of base, and the residue then crystallised from chloroform, in which it is only very slightly soluble. Crystallisation was repeated from this solvent until the melting point was constant at 120—120·5°.

0·2009 gave 12·9 c.c. of moist nitrogen at 14° and 734 mm. N = 7·29.
0·2013 „ 12·6 „ „ „ 13° „ 744·5 mm. N = 7·24.
$C_{10}H_{13}O_3N$ requires N = 7·18 per cent.

Glyceryl-p-*toluidide* (*Active*).

This was similarly prepared and purified by crystallisation from chloroform. The constant melting point was 131—131·5°.

0·1001 gave 6·5 c.c. moist nitrogen at 23° and 754·8 mm. N = 7·27.
0·2009 „ 12·9 c.c. „ „ 14° „ 734 mm. N = 7·28.
$C_{10}H_{13}O_3N$ requires N = 7·18 per cent.

d 140°/4° = 1·1735. d 150°/4° = 1·1643.

Rotation of Glyceryl-p-*toluidide.*

Temp.	Length of tube.	d $t°/4°$.	α_D.	$[\alpha]_D$.	$[M]_D$.
179°	49·92 mm.	1·1376	−16·82°	−29·62°	−57·76
136	„	1·1772	−19·03	−32·38	−63·14
109	„	1·2020	−20·41	−34·02	−66·34
98	„	1·2121	−20·99	−34·69	−67·65
[20° calculated from rotations at 98° and 136° above				−39·43	−76·89]

V. *Rotation of Glycerylanilide and of Glyceryl*-o- *and* -p-*toluidide in Methyl Alcohol Solution.*

Owing to the impossibility of taking the rotation of the fused glyceryl-*o*-toluidide, it was determined in solution, the rotation of the

p-compound and of the glycerylanilide and amide being also determined under the same conditions for the purpose of comparison.

The glycerylanilide is only soluble in methyl alcohol to the extent of a little more than 6 per cent., and the glyceryl-*p*-toluidide to the extent of 6·61 per cent., so the rotations were determined in solutions of about 2·5, 5, and 6 per cent. concentration respectively.

In benzene, glycerylanilide is only soluble to the extent of 0·15 per cent. Glycerylamide is even less soluble in methyl alcohol than the other compounds, and hence could only be optically examined in the two lower concentrations.

Rotation in methyl alcohol solution at 20° ($l = 100{\cdot}45$ *mm.*).

Weight of solution, grams.	Weight of substance, grams.	Grams substance in 100 grams solution.	d 20°/4°.	$\alpha_D^{20°}$.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.
		*Glycerylamide.**				
8·1877	0·1997	2·4390	0·8022	−1·24°	−63·09°	−66·24°
7·7469	0·3689	4·7619	0·8122	−2·40	−61·77	−64·86
[Rotation in liquid state (calculated) $[\alpha]_D^{20°} = -44{\cdot}14°$, $[M]_D^{20°} = -46{\cdot}35°$].						
		Glycerylanilide.				
10·2500	0·2500	2·4390	0·8035	−1·42°	−72·13°	−130·55°
10·5000	0·5000	4·7619	0·8118	−2·70	−69·53	−125·85
10·6000	0·6000	5·6604	0·8155	−3·12	−67·29	−121·79
[Rotation in liquid state (calculated) $[\alpha]_D^{20°} = -47{\cdot}82°$, $[M]_D^{20°} = -86{\cdot}55°$].						
		Glyceryl-p-toluidide.				
10·2500	0·2500	2·4390	0·8039	−1·26°	−63·97°	−124·74°
10·5000	0·5000	4·7619	0·8108	−2·49	−63·95	−124·70
10·6000	0·6000	5·6604	0·8140	−2·95	−63·74	−124·29
[Rotation in liquid state (calculated) $[\alpha]_D^{20°} = -39{\cdot}43°$, $[M]_D^{20°} = -76{\cdot}89°$].						
		Glyceryl-o-toluidide.				
10·2500	0·2500	2·4390	0·8025	−0·64°	−32·55°	−63·47°
10·5000	0·5000	4·7619	0·8117	−1·37	−35·41	−69·05
10·6000	0·6000	5·6604	0·8137	−1·72	−37·18	−72·50

* A 6 per cent. solution could not be prepared, owing to the limited solubility.

VI. *Molecular Volumes.*

In the following table, the experimental molecular volumes are compared with the values calculated by Traube's formula:

	Molecular volume at 15°. Calculated.	Experimental.
Glycerylamide.....	85·1	$\frac{105}{1·4053} = 74·7$
Glycerylanilide	143·7	$\frac{181}{1·2806} = 141·3$
Glyceryl-*p*-toluidide ...	159·8	$\frac{195}{1·2885} = 151·3$

Constants used:

C = 9·9; H = 3·1; O (in CO) = 5·5; O (in OH) = 0·4; N‴ = 1·5.
Co-volume = 25·9; deduction for benzene ring = 13·2.

Thus in the case of all three compounds the molecular volume points to association, which is greatest in that of the amide and least in that of the anilide.

In carrying out this investigation we have been assisted by funds placed at the disposal of one of us by the Government Grant Committee of the Royal Society.

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Birmingham.

XXVI.—*The Preparation of Acetylchloraminobenzene and some related Compounds.*

By F. D. Chattaway and K. J. P. Orton.

The criticism to which Armstrong (Trans., 1900, 77, 1047) has recently subjected our work makes it evident that several points need fuller consideration.

In a reference which he makes to the omission in our earlier papers of all mention of Slossen's work (*Ber.*, 1895, 28, 3265), he fails to remark that we have twice expressed our regret (Proc., 1900, 16, 2, and Trans., 1900, 77, 134) that at the time these papers were published we had unfortunately overlooked the communication and were consequently in entire ignorance of it. Whilst very gladly acknowledging Slossen's contribution to the subject, we may perhaps again repeat that our observations were made quite independently.

Armstrong also notes in our papers the absence of all reference to

his views upon substitution. In his first communication to the Society on the subject (Trans., 1887, 51, 258), he advocates the view originally put forward by Kekulé that in all cases of substitution additive compounds are first formed by the union of the interacting substances. He endeavours to develop a general theory, and writes: "Passing now to the consideration of the formation of di-derivatives, I may at once point out that the difference under discussion in the behaviour of the two classes of mono-derivatives * is, in my opinion, attributable to the different manner in which they form additive compounds. In the case of those which furnish the ortho- and para-derivative, it may be held that the additive compound results from the union of the reacting molecule with the carbon atom to which the radicle R′ is attached" —and again: ". . . . my opinion being that the additive compound which generates the meta-derivative is formed by the combination of the reacting molecule *with the radicle* R′ of the mono-derivative, and not with the carbon atom which carries that radicle." †

Forster Morley, in reply (Trans., 1887, 51, 579; Proc., 1887, 3, 61), directed Armstrong's attention to the case of the anilines, and instancing their behaviour on nitration, insisted that his assumptions as to the particular atoms where addition takes place were opposed to known facts and "in the very highest degree improbable." ‡

After considering these objections, Armstrong, although he does not in any way withdraw his previously quoted generalisations, appears to have modified his views, for in his answer (Trans., 1887, 51, 583) he states: "The behaviour of amido- and hydroxy-derivatives, which is in many respects peculiar, deserves minute study from the above point of view, several highly suggestive observations having been recorded, from which it may be inferred that the phenomena of

* The formation of para- and ortho- and of meta-derivatives respectively.

† Armstrong earlier in the paper refers to the facts that potassium phenyl sulphate on heating becomes potassium phenol-*p*-sulphonate, and that the nitrosamine of methylaniline is converted by digestion with an alcoholic solution of hydrogen chloride into *p*-nitrosomethylaniline, not as in any way throwing doubt on his theory, but as showing that where para-compounds are produced it is not necessary to assume that the reacting molecule attaches itself to the carbon atom occupying the para-position relatively to the one to which the radicle R′ is attached. He also refers to the transformations of sodium and potassium phenyl carbonates as instances, among others, showing that the proportion in which ortho- and para-derivatives are formed varies with the nature of the transforming compounds.

‡ Forster Morley pointed out that, if Armstrong's views were correct, compounds containing the NH_2 group, which can combine with nitric acid, ought to produce meta-derivatives, whilst the chief product when aniline, for example, is nitrated is *p*-nitroaniline. He argued that when aniline yields a meta-derivative on nitration in presence of a large excess of sulphuric acid, it is the circumstance that the nitric acid, HNO_3, cannot then combine with the NH_2 group which causes the formation of the meta-compound. This explanation, which is now generally accepted is the exact opposite of Armstrong's view.

substitution are less simple than is perhaps commonly supposed, and that isomeric change is by no means of infrequent occurrence in the formation of derivatives of amines and phenols." He then mentions several well-known cases of isomeric change, among them the transformation of acetylchloraminobenzene, of the nitrosamine of methylaniline and of potassium phenyl sulphate, and adds: "These examples, although few, are perhaps numerous enough to justify the inquiry whether the formation of para-derivatives of primary or secondary amines and of phenols is not always preceded by that of an isomeric compound formed by the displacement of the aminic or hydroxylic hydrogen. Whether ortho-derivatives are formed in a similar manner remains to be ascertained . . . ."

Since 1887,* much work throwing great light on the mechanism of substitution has been done. For example, Bamberger (*Ber.*, 1894, **27**, 359; 1895, **28**, 399; 1897, **30**, 1248, 2247) has shown that nitroamino-derivatives of benzene are transformed readily into *o*- and *p*-nitroanilines, and that phenylsulphamic acid easily passes into *o*- and *p*-sulphanilic acids. Hantzsch (*Ber.*, 1897, **30**, 2334) also has shown that in brominated diazonium chlorides the chlorine can exchange places with bromine atoms in those positions. These facts clearly demonstrate that the NO_2 group and halogen atoms when associated with a nitrogen atom can readily interchange with hydrogen atoms in the nucleus in ortho- and para-positions relatively to the carbon atom to which the nitrogen atom is attached, and in these only. It had been shown much earlier that CH_3 and C_2H_5 groups could wander from the nitrogen of secondary anilines only into these positions in the ring (Hofmann, *Ber.*, 1874, **7**, 526; Limpach, *Ber.*, 1888, **21**, 641).

In 1899 we submitted to the Chemical Society a paper in which our views on the substitution of chlorine and bromine in anilines and anilides were clearly stated, accompanied by the experimental evidence on which we based them. This paper was read on June 1st, and an abstract of it containing all our experimental results, which admitted but of one explanation, was printed in the Proceedings of that date (Proc., **15**, 152). In the next number of the Proceedings, containing an account of the meeting of June 15th (Proc., **15**, 176), Armstrong published a short note containing an unreserved withdrawal of his previous opinions, and a substitution of views in the main identical with those to which our work had led us, all the important facts of

* Bender in 1886 (*Ber.*, **19**, 2272), a year before the appearance of Armstrong's first paper, showed that the chlorine in acetylchloraminobenzene easily passes into the para-position in the nucleus, and this observation was extended in 1890 by Comstock and Kleeberg (*Amer. Chem. J.*, **12**, 500), who proved that the iodine atom in formyliodaminobenzene behaves similarly.

this work having been published a fortnight previously. Armstrong's more complete communication to the British Association was made two months later. In neither place does he refer to our work, although his changed views are as direct a consequence of it as of the work of Bamberger, of Hantzsch, and of others.

We have never in any way claimed originality for the view that substitution is probably preceded by the formation of an isomeride which subsequently undergoes isomeric change; this directly follows from much earlier work. What we do claim is that in the particular case of the substitution of halogen in anilines and anilides we have converted a probability into a certainty by showing that all the compounds ordinarily formed by substitution can be produced by isomeric change from previously formed nitrogen chlorides and bromides, and that the degree of difficulty with which transformation is effected corresponds with that experienced in effecting apparently direct substitution.

Experimental.

Acetylchloraminobenzene.

Armstrong (Trans., 1900, **77**, 1051), referring to our method of preparing acetylchloraminobenzene from acetanilide, states: "According to my experience, whatever excess of hypochlorite be taken, and however long the stirring be continued, the chlorination is almost always imperfect, and eventually at most 60—70 per cent. of *p*-chloracetanilide has been obtained."

We have in consequence reinvestigated our original method, namely, the action of a solution of bleaching powder on acetanilide suspended in excess of potassium bicarbonate solution.

A mixture of finely powdered acetanilide and potassium bicarbonate was added to an excess of a 0·3*N* solution of bleaching powder. After standing for some hours at the ordinary temperature, the solid was filtered off and thoroughly extracted with chloroform, in which both acetanilide and the nitrogen chloride are soluble. After the solution had been dried by calcium chloride, the solvent was completely evaporated away in a vacuum. An analysis, made by titrating the iodine set free from acidified potassium iodide by a weighed quantity of the solid residue, showed it to be pure acetylchloraminobenzene.

0·1126 liberated I = 13·25 c.c. *N*/10 iodine. Cl as : NCl = 20·86.
$C_6H_5 \cdot NCl \cdot CO \cdot CH_3$ requires Cl as : NCl = 20·9 per cent.

In our later work (Trans., 1900, **77**, 789, &c.), we have used a solution of potassium hypochlorite containing potassium bicarbonate* for

* Prepared by mixing solutions of potassium bicarbonate and bleaching powder and filtering off the calcium carbonate.

the preparation of chloramino-derivatives, when it was necessary to avoid the presence of acids. With this agent, pure acetylchloraminobenzene is very easily and rapidly prepared in any quantity.

Twenty grams of acetanilide were added to 300 c.c. of a solution of potassium hypochlorite (0·3 to 0·4 *N*) containing potassium bicarbonate. After standing for half an hour at the ordinary temperature of the laboratory, some of the solid was filtered off, washed with water, and dried in a vacuum over sulphuric acid. The product was well crystallised in small plates.

0·1655 liberated I = 18·45 c.c. *N*/10 iodine. Cl as : NCl = 19·8 per cent.

Further portions of the solid were filtered off at intervals, dried, and analysed:

After 3 hours the product contained Cl as: NCl = 20·26 per cent.
„ 5 „ „ „ Cl as: NCl = 20·81 „ „

It is seen, therefore, that in half an hour more than 95 per cent. of the acetanilide becomes converted into the chloramino-derivative, and that the conversion is finally absolutely complete. We do not find it an advantage to work at the higher temperature recommended by Armstrong.

It must be carefully noted that a too concentrated solution of bleaching powder cannot be used. If potassium bicarbonate is added to a solution of bleaching powder above 0·5 *N*, chlorine is always set free, no matter what excess of bicarbonate is present. Under such circumstances, we find that *p*-chloroacetanilide is invariably formed. If a sufficient excess of bleaching powder is employed, the whole of the acetanilide will become converted into *p*-chloroacetanilide, and this, in its turn, into its chloramino-derivative.

Five grams of acetanilide were mixed with a considerable quantity of potassium bicarbonate and added to a large excess of a normal solution of bleaching powder. Free chlorine was liberated, and was unmistakably present in the carbon dioxide evolved. After standing for 3 days, the solid was filtered off and extracted with chloroform. The residue left, after evaporating away the chloroform, was pure acetylchloramino-*p*-chlorobenzene.

0·2395 liberated I = 23·5 c.c. *N*/10 iodine. Cl as : NCl = 17·39.
$C_6H_4Cl{\cdot}NCl{\cdot}CO{\cdot}CH_3$ requires Cl as : NCl = 17·38.

We have never observed the formation of *p*-chloroacetanilide when no chlorine is developed; moreover, acetylchloraminobenzene has been kept completely unchanged for a week under dilute hypochlorite solution, and apparently may be so kept for a long period.

Acetylchloraminobenzene, from whatever solvent it separates,

crystallises, according to our observations, in plates or short, four-sided prisms. When needles are present, they are undoubtedly the isomeric *p*-chloroacetanilide, and can be shown not to be the nitrogen chloride by the following method. The crystals are placed on a slide under a microscope and a few drops of a strong solution of potassium iodide added. The needles of anilide remain untouched, whilst the plates and prisms of the chloramino-compound vigorously react with the iodide, and melt to an oil which afterwards solidifies. This substance is readily obtained in large plates melting at 92° from a mixture of chloroform and petroleum (b. p. 50—80°), which we still believe to be the best solvent. It dissolves easily in cold glacial acetic acid, and by adding water may be reprecipitated in a pure state as small plates or prisms. When it is dissolved in hot dilute acetic acid, needles of *p*-chloroacetanilide frequently separate, as we have noted.* We have, however, also recrystallised it from dilute acetic acid, although we do not regard this as a suitable solvent.

Armstrong has taken exception to our statement concerning the *general reaction* with alcohol of substances containing the nitrogen halogen linking. We were not referring in this statement to the *transformation* which acetylchloraminobenzene undergoes under certain circumstances in alcoholic solution. This transformation had already been observed by Bender. Owing to the readiness with which all such substances react with alcohol, and in some cases undergo transformation when dissolved in it, we cannot recommend it as a solvent.

Some other observations of Armstrong will be more appropriately considered at another time.

Benzoylchloraminobenzene.

As a confirmation of our previous observations, we have again prepared this substance in order to show that benzanilide also is completely transformed into its chloramino-derivative by a dilute solution of potassium hypochlorite in the presence of bicarbonate. The reaction is very much slower than in the case of acetanilide. After 3 days standing, some of the solid was filtered off, dried, and analysed, and shown to be pure benzoylchloraminobenzene.

0·1474 liberated I = 12·75 c.c. *N*/10 iodine. Cl as : NCl = 15·33.
$C_6H_5 \cdot NCl \cdot CO \cdot C_6H_5$ requires Cl as : NCl = 15·33 per cent.

After another week's standing, it was found that the substance had

* Bender describes it as separating in needles from this solvent. He does not give the melting point of these needles ; most probably they were *p*-chloroacetanilide, which invariably crystallises in this form.

undergone no change, and on analysis it again gave Cl as : NCl = 15·33 per cent.

Acetylchloramino-2 : 4-dichlorobenzene.

Hitherto this substance has been obtained by Witt, Jackson and Wing,* and us, by the action of bleaching powder on an acetic acid solution of acetanilide or 2 : 4-dichloroacetanilide. From this method of preparation it might be inferred that it could only be formed through the agency of hypochlorous acid. We find, however, that it can very easily be prepared by the direct action of chlorine.

Acetanilide (1 part) is dissolved in glacial acetic acid (4 parts) and excess of anhydrous sodium acetate is added. Dry chlorine gas is then led into the cooled solution until no more is absorbed. On adding water, the nitrogen chloride separates as an oil which rapidly solidifies. It can be obtained pure by one crystallisation from petroleum. In the absence of sodium acetate, although some acetylchloramino-2 : 4-dichlorobenzene is always formed, the conversion of the 2 : 4-dichloroacetanilide into the nitrogen chloride is not perfect, owing to the liberation in the reaction of free hydrochloric acid.

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XXVII.—*The Preparation of Esters from other Esters of the same Acid.*

By T. S. PATTERSON and CYRIL DICKINSON.

SOME time ago we commenced some experiments with the object of preparing methyl ethyl tartrate, a comparison of the rotation of which with that of methyl and of ethyl tartrate could not fail to be interesting. In this work we were encouraged by the hope that methyl ethyl tartrate would prove to be a solid at the ordinary temperature, in which case its purification would present no great difficulty. Our first attempt to prepare it was made by boiling tartaric acid with ethyl alcohol for some hours, then removing the excess of alcohol first by distillation and afterwards by the evaporation of the residue in a vacuum over sulphuric acid. The very viscous substance thus obtained (83 grams) was then dissolved in excess of methyl alcohol (100 grams) and the solution saturated with hydrogen chloride. After removal of the

* This substance, as already noticed by us, was not obtained by these chemists in a pure state, but was regarded by them as a liquid additive product with hypochlorous acid.

alcohol and hydrogen chloride and distillation of the residue under low pressure, the ester obtained had a rotation of $+5{\cdot}72°$ ($l=2$, $t=17°$), that is to say, consisted of nearly pure methyl tartrate.

The method of preparation was therefore modified. One hundred grams of tartaric acid, after being dried and powdered, were heated in a flask under a reflux condenser with 25 grams of methyl alcohol (the calculated quantity being 22 grams) on a water-bath for about 8 hours. The acid ultimately went into solution. The syrup after cooling was then saturated with hydrogen chloride, after which 33 grams (calc. 31 grams) of ethyl alcohol were added and hydrogen chloride again passed into the solution to saturation and the mixture allowed to stand overnight. The ester obtained after removal of the excess of alcohol and hydrogen chloride and distillation of the residue under reduced pressure was found to boil at 144—152° (bath 190—210°, pressure about 12 mm.) and weighed 50 grams. It had a rotation of $+11{\cdot}14°$ ($l=2$, $t=18°$).

This substance was then redistilled under reduced pressure. It boiled at 157—158° (bath 194—197°, pressure 15 mm.). Three fractions were collected, the first being only a small one. The rotation of the second was $+10{\cdot}9°$ and of the third $+11{\cdot}0°$ ($l=2$, $t=15°$).

This is approximately intermediate between the rotations of methyl tartrate and ethyl tartrate, so that the substance obtained was probably composed mainly of methyl ethyl tartrate, but it showed no tendency to crystallise nor did any solid separate out when a few crystals of methyl tartrate were added. No further purification could be expected by distillation, and as any other method, except crystallisation, would probably involve more labour than the result would justify and, in addition, be still uncertain, the attempt to prepare this substance in a pure condition has been for the present abandoned.

The result of the first experiment, however, seemed interesting enough to warrant further investigation, since it appeared from it that ethyl hydrogen tartrate had been almost completely converted into methyl tartrate by the action of methyl alcohol and hydrogen chloride.

Now in certain cases the preparation of an ester from the acid and the alcohol presents difficulties which could be overcome by the use of another ester in place of the acid. It is therefore of importance to ascertain whether such a method will yield a pure product.

Preparation of Ethyl Tartrate from Methyl Tartrate.

This was carried out by the method recommended by Fischer and Speier (*Ber.*, 1895, **27**, 3252), except that methyl tartrate was substituted for the acid.

Hydrogen chloride was passed into 120 grams of ethyl alcohol until

5 grams had been absorbed; 30 grams of methyl tartrate were then added, and the mixture boiled for about 4 hours under a reflux condenser. The alcohol and hydrogen chloride were then removed, and the ester remaining was distilled in a vacuum. Three fractions were collected, the last of which had an observed rotation of $+8{\cdot}498°$ ($l=1$, $t=18{\cdot}6°$). Under the same circumstances, pure ethyl tartrate would have a rotation of $+9{\cdot}15°$. Since pure methyl tartrate has a rotation of about $+2{\cdot}8°$ at the same temperature, and we may assume without any great error that the rotation of a mixture of ethyl and methyl tartrates is the sum of the rotations of each constituent separately, it follows that about 90 per cent. of the original methyl tartrate had been converted into ethyl tartrate.

The three fractions of impure tartrate were then mixed and treated anew with 120 grams of ethyl alcohol containing 5 grams of hydrogen chloride. After the alcohol and hydrogen chloride had been removed and the ester fractionated several times, a product was obtained having a rotation of $+9{\cdot}25°$ ($l=1$, $t=18{\cdot}8°$), which is exactly the same as that of pure ethyl tartrate. It is thus clear that methyl tartrate may be completely converted into ethyl tartrate by the method described.

The reverse reaction was then tried.

Preparation of Methyl Tartrate from Ethyl Tartrate.

Sixty grams of methyl tartrate were boiled for about 5 hours with 240 grams of methyl alcohol containing 15 grams of hydrogen chloride. On subsequent removal of the alcohol and distillation of the residue in a vacuum, a very viscous liquid was obtained of observed rotation $+6{\cdot}249°$ ($l=2$, $t=16{\cdot}5°$), so that about 87 per cent. of the ethyl tartrate had been converted into methyl tartrate. Instead of treating this again with methyl alcohol and hydrogen chloride, a few small crystals of methyl tartrate were added. By next morning, the ester had almost completely solidified, only a small quantity of liquid refusing to crystallise. The whole mass was spread on porous earthenware. When dry, the solid weighed 37 grams. This represents a yield of 71 per cent. on the 60 grams of ethyl tartrate used, which, considering the loss of methyl tartrate incurred in the removal of a first fraction in distillation, and of the portion dissolved in the ethyl tartrate which was absorbed by the porous plate, agrees as well as could be expected with the 87 per cent. found polarimetrically.

The substance obtained was then dissolved in benzene and allowed to crystallise; 22 grams separated out. The crystals were dried on porous earthenware and then distilled. After the first small fraction had been removed, the residue boiled at 150° (bath 175°, pressure about

15 mm.). The distillate soon solidified; its melting point was not very sharp, and lay at 55—56°, which is considerably higher than that usually given, namely, 48°. Its density, relative to water at 4°, was examined at various temperatures, the following figures being obtained:

Temperature	29°	39·8°	58·2°	77·3°
Density	1·3187	1·3074	1·2878	1·2676

These figures plotted relatively to temperature are found to lie upon a straight line. By extrapolation, the density at 20° is found to be 1·3286, Pictet (*Jahresber.*, 1882, 856) giving 1·3284, and at 100°, 1·2433, Pictet giving 1·2500.

As the rotation of methyl tartrate appears to have only been examined at 18°, 20°, and 100°, we have obtained the following figures for the rotation of this specimen at intermediate temperatures, from which a curve may easily be constructed.

$t°$.	Rotation (100 mm.).	Density.	$[\alpha]^{t}_{D}$.
18·2	+2·910°	1·3306	+2·19°
12·7	2·250	1·3363	1·68
36·1	4·766	1·3113	3·63
99	8·063	1·2444	6·48
82·1	7·580	1·2624	6·00
79·8	7·475	1·2649	5·91
71·4	7·025	1·2738	5·51
64·2	6·650	1·2815	5·19
58·6	6·305	1·2874	4·90
52·5	5·958	1·2937	4·61
28·1	4·030	1·3198	3·05

Since, from the experiments described above, it appears that methyl tartrate can be converted into pure ethyl tartrate, and *vice versâ*, by Fischer's method, and as the first experiment mentioned shows that the same change can be accomplished by the saturation method at a low temperature, it seems probable that any other ester may be obtained in a pure condition by an analogous process, it being best, of course, to choose as starting point a substance whose physical condition is different from that of the ester which it is desired to prepare.

YORKSHIRE COLLEGE,
LEEDS.

XXVIII.—*Note on Tecomin, a Colouring Matter derived from the Heart-Wood of Bignonia Tecoma.*

By Theodore H. Lee.

Bignonia Tecoma is a fairly common tree in the uplands of Minas, Brazil. When full grown, it is about thirty feet high to the first branches; the crown is umbrella-shaped and a further twenty feet high. The bark is smooth and the trunk usually crooked. In September, just before the rains set in, *B. Tecoma* is a very striking object, as it is covered with a mass of brilliant yellow flowers resembling the azalea, and showing up all the more strongly on account of the absence of leaves, which do not appear till later.

The tinctorial properties of the wood have long been known to natives, who mix the sawdust and shavings with slaked lime, and heat the mass with water. The resulting bath is used to dye cotton cloth. A paste of lime and the sawdust with water is used to stain lighter coloured woods a deep brown.

The writer's attention was recently drawn to the fact that, on rubbing the sawdust with soap and water, a pink colour was developed. Preliminary experiments showed that a yellow colouring matter was contained in the wood, which was coloured red by alkalis, and a clearer yellow by acids.

Fifty grams of the sawdust were exhausted by 85 per cent. alcohol and the combined alcoholic filtrates concentrated to about 100 c.c. in a retort. On transferring to a dish and cooling, a plentiful crop of shining chrome yellow crystals with a nacreous lustre appeared. These were collected, washed with cold alcohol, and dried between blotting-paper.

The filtrate was evaporated to a paste, taken up with aqueous ammonia, boiled, and filtered to separate a resinous residue. The ammoniacal filtrate, which is of a magnificent crimson colour, was acidified with hydrochloric acid, the dull yellow precipitate washed, extracted with hot alcohol, filtered, and the alcohol evaporated. A further crop of the yellow crystals was obtained; these, however, were of a darker colour than the first, and required recrystallising from alcohol to free them from traces of resin, which is obstinately retained. The yield of the yellowing colouring matter was approximately 5 per cent. Of the resin, 2 per cent. was separated, and a further quantity remained in the mother liquor from the second crystallisation. A small quantity of the yellow dye, provisionally named *tecomin*, is retained in this mother liquor, but the amount is small, as

the colour reaction with alkalis is almost masked by the brown colour of the resin.

From the sawdust which has been exhausted by alcohol, hot dilute caustic soda extracts a deep brown dye (which is that utilised by the natives). It is precipitated by acids as a flocculent, brown solid, soluble in alcohol, from which it separates on evaporation as an amorphous mass. It is slightly sensitive to alkalis probably on account of a little tecomin retained. The crystallised tecomin is not very soluble; a saturated solution in 85 per cent. alcohol contains about 0·8 per cent. of it. When a couple of drops of this solution are let fall into 50 c.c. of water, a faint opalescence is produced. On addition of a drop of a dilute mineral acid, the solution clears and takes a pale yellow tint. A little alkali changes this to a full rose-colour.

Weak acids do not affect tecomin, which therefore can be used in the cold for titrating carbonates, silicates, sulphides, sulphites, borates, and cyanides.

Organic acids affect the colour reaction, but indefinitely. Solutions of acetates, oxalates, citrates, &c., are alkaline in their reaction, and the red colour is discharged slowly by strong acids, but the end-point is indistinct.

The indicator answers excellently for alkalimetry, using the alkalis, alkaline earths, and mineral acids as reagents. Calcium, barium, and magnesium carbonates react with the yellow solution, giving the red colour. The sensitiveness is extreme. In a bulk of 50—70 c.c. coloured with two drops of the alcoholic solution, 0·2 c.c. of $N/100$ acid or alkali causes a sharp end reaction.

Morro Velho,
Minas, Brazil.

XXIX.—*Iron Nitride.*

By Gilbert John Fowler, M.Sc. (Vict.).

Although the chemistry of the nitrides is of considerable interest from many points of view, little is definitely known concerning these compounds. Since the discovery of azoimide, which reacts with metals to form a class of nitrides, it became of interest to compare the properties of the latter with nitrogen compounds of the metals obtained by other means. Iron nitride, from its fairly easy decomposability, appeared likely to present some interesting reactions and possibly to allow of a determination of its heat of formation.

The earliest work on the combination of iron and nitrogen was

done by Berthollet, and by Thénard (*Traité de Chimie*, 1834, i, 434), who allowed ammonia to act on iron wire at a red heat and found that the weight of the iron scarcely increased, but that the metal became brittle.

Savart (quoted by Stahlschmidt, *Pogg. Ann.*, 1865, **125**, 37) mentioned that after ammonia had passed over iron for a long time the metal became softer, whilst after an action of only two hours it behaved like steel and could be hardened.

These observers did not recognise the formation of iron nitride.

According to Despretz (*Ann. Chim. Phys.*, 1829, **42**, 122), iron increased in weight from 7 to 11·5 per cent. by heating in ammonia and changed to a white, brittle mass, which he recognised as a compound of iron and nitrogen.

Buff (*Annalen*, 1852, **83**, 375) found an increase of 6 per cent. and Régnault of 12 to 13 per cent. in this reaction.

Fremy (*Compt. rend.*, 1861, **52**, 322) prepared iron nitride by heating anhydrous ferrous chloride in a stream of dry ammonia. The compound thus obtained, according to Fremy, contained 9·3 per cent. of nitrogen, from which he calculated the formula Fe_5N_2. The 11·5 per cent. of nitrogen found by Despretz corresponded to that required for the formula Fe_2N.

From these results, it might be concluded that nitrogen, like carbon, was able to combine with iron in several proportions to form compounds which would alloy with free iron. Stahlschmidt (*loc. cit.*), however, came to the conclusion that nitrogen combines with iron in a perfectly definite ratio to form a substance of the formula Fe_2N, and that all the nitrides previously prepared containing less nitrogen than required by this formula must be looked upon as mixtures of this nitride of definite composition with pure iron.

According to Rogstadius (*J. pr. Chem.*, 1862, **86**, 307) and Briegleb and Geuther (*Annalen*, 1862, **123**, 228), finely divided iron prepared from ferrous oxalate or by the reduction of ferric oxide in hydrogen, takes up about 2 per cent. of nitrogen at the ordinary temperature or by continuous heating in nitrogen. Stahlschmidt was not able to prepare iron nitride in this way.

By the electrolysis of a mixture of a ferrous salt and sal ammoniac, a shining or spongy mass separates which, according to Krämer (*Arch. Pharm.*, 1861, [ii], **105**, 284), is an iron nitride containing 1·5 per cent. of nitrogen; according to Meidinger (*Dingl. Polyt. J.*, 1863, **168**, 283), it is an iron ammonium alloy. The substance is said to give off a smell of ammonia and liberates hydrogen from boiling water.

It should be mentioned, finally, that Allen (*Chem. News*, 1880, **41**, 231), by heating soft iron wire in ammonia, obtained a product con-

taining $2\frac{1}{2}$ per cent. nitrogen, and concluded, from comparison of the behaviour of this compound with iron and steel containing nitrogen, that this element existed in iron and steel combined with the iron to form nitride.

The experiments on iron nitride described in the present paper may be divided under the following heads :—

1. Preparation.
2. Analysis.
3. Determination of physical properties.
4. Investigation of action of various reagents on the substance.
5. Determination of the temperature of decomposition and heat of formation of iron nitride (see Fowler and Hartog, this vol., p. 299).

The experiments have confirmed the results of Stahlschmidt in almost every particular, and various new facts have been ascertained, conclusions from which have been dealt with below.

Preparation of Iron Nitride.

This was accomplished by three methods :

(*a*) By the action of ammonia on ferrous chloride or bromide.

(*b*) By the action of ammonia on finely divided iron.

(*c*) By the action of ammonia on iron amalgam.

Preparation of Ammonia.—As large quantities of ammonia were required in this research, a ready method of preparing the gas pure and dry was necessary. The best plan was found to be a modification of one described by Neumann (*J. pr. Chem.*, 1888, [ii], 37, 342). A strong solution of ammonia (sp. gr. 0·88) is allowed to drop from a tap funnel upon solid caustic soda contained in a glass tower, from the bottom of which the solution of the alkali can be drawn off from time to time. It was found best to place a pad of glass wool under the end of the tap funnel, as the evolution of ammonia is apt to be too violent if the solution is allowed to fall directly on to the caustic soda. The ammonia gas, thus evolved in a fairly dry state, from contact with the solid caustic soda, was passed through three towers, filled partly with sticks of caustic potash and partly with granulated soda lime which had been previously heated.

The gas, after passing through the tube in which the nitride is prepared, was led into an ordinary nitrogen measuring tube containing hydrochloric acid, which is prevented by mercury from being sucked back. By this means, it was easy to see when the ammonia was free from air and also to note the progress of the reactions described below.

(a) *Action of Ammonia on Ferrous Chloride.*—The course of the reaction was carefully observed, especially with a view to discover whether any hydrazine derivatives were formed. The ferrous chloride,

prepared by heating iron wire to redness in a current of hydrogen chloride (the unattacked iron was removed by means of a magnet) was submitted to the action of ammonia at various temperatures up to the melting point of lead, and the products of the reaction, both solid and gaseous, were examined. The course of the reaction appears to be as follows (Fowler, *Chem. News*, 1900, 82, 245).

At low temperatures, one mol. of ferrous chloride rapidly absorbs six mols. of ammonia to form a voluminous white mass which gives off ammonia again at a temperature of 100°. On further heating reduction of the ferrous chloride takes place, resulting in the formation of ammonium chloride, iron nitride, and a small quantity of nitrogen. No formation of hydrazine compounds or other intermediate products could be observed. To prepare the nitride in quantity by this method a temperature of about 600° appears to be necessary.

Ferrous Bromide was prepared and similarly treated, the temperature of reaction was not sensibly lowered and the products of analysis were analogous (Fowler, *loc. cit.*).

In appearance, the nitride obtained from either ferrous chloride or bromide was sometimes like that obtained from reduced iron; at other times, when a higher temperature was used, it was obtained in silvery pellicles as described by Stahlschmidt and others. It was found difficult to obtain it in quantity free from intermixed ferrous and ammonium chloride or bromide; it was therefore thought better to prepare the nitride directly by the interaction of iron and ammonia.

(b) *Preparation of Iron Nitride by Interaction of Iron and Ammonia.*—For this purpose, iron reduced from the oxide obtained by precipitation and drying was found to be most suitable. As this iron tends to be pyrophoric, it was found necessary to complete the reduction of the oxide in hydrogen and the conversion of the iron into nitride without exposure to air. Ferric hydroxide is reduced by hydrogen in a wide glass tube to each end of which narrower glass tubes are fused which can be readily connected up with the ammonia apparatus and measuring tube outside the furnace. One of the narrower tubes is bent in such a way that this part of the apparatus can be conveniently detached and suspended on the balance. The hydroxide must be heated in hydrogen until no further loss of weight occurs, as it is found that if the reduction is not complete, subsequent heating in ammonia at a temperature sufficient to form nitride is not sufficient completely to reduce the oxide of iron. The last portions of oxide mixed with a large excess of iron apparently require a higher temperature for their reduction. It was found in one case, in which care had not been taken to completely reduce the oxide in hydrogen, that, after heating in ammonia until no further increase in weight occurred, there was still a large amount of oxide present, as evidenced by the fact that

a black, insoluble residue consisting probably of magnetic oxide was left on treating with dilute acid, and also that on heating further in ammonia at a higher temperature water was given off. As this steam decomposes iron nitride, the presence of oxide of iron acts prejudicially to the formation of the latter.

When the iron is once reduced, it is important that air be as far as possible excluded until it has been completely converted into nitride. By using pinchcocks upon the indiarubber connections, it is possible to connect and disconnect the tubes and insert stoppers without admitting an appreciable amount of air. After each weighing, the contents of the tube were shaken so as to expose a fresh surface.

The best temperature for the preparation of iron nitride is that stated by Stahlschmidt, namely, just above the melting point of zinc (414°). At this temperature, hydrogen is rapidly given off on passing ammonia over finely divided iron. The almost complete cessation of the evolution of hydrogen shows the reaction to be complete.

If the temperature is raised, it is found, in confirmation of Stahlschmidt's results, that the percentage of nitrogen in the nitride decreased, even if ammonia be passing over. This is explained by the fact that iron nitride is decomposed by hydrogen at the same temperature as that at which it is formed, ammonia being again produced. On raising the temperature, the percentage of hydrogen in the gas above the substance is increased by dissociation of the ammonia, and the tendency is for it to take up nitrogen from the nitride. By allowing hydrogen to pass over the nitride heated in a tube, Stahlschmidt showed (*loc. cit.*, p. 47) that ammonia is re-formed at this temperature, and this result was confirmed. As soon as the temperature of the furnace reached approximately that at which nitride is formed, ammonia was evolved, and recognised by its precipitating Nessler's solution, placed in connection with the end of the apparatus.

The temperature of formation in ammonia, and decomposition in hydrogen, of the nitride being the same, the preparation of the compound is difficult and tedious, and some practice is needed to keep the current of ammonia passing at a sufficient pace, as, if hydrogen is allowed to accumulate, the formation of nitride ceases.

It was at first thought that this reaction might be a suitable one to study quantitatively at different temperatures as an example of mass action. The temperature, however, at which the reaction takes place, and that at which ammonia is dissociated in presence of a surface such as powdered iron affords (Ramsay and Young, Trans., 1884, 45, 88), are too close to admit of satisfactory results being obtained. It was found indeed, that even at the temperature of the experiment some ammonia is in all probability dissociated. Some of the gas, after

passing over the iron and iron nitride formed, was collected in the nitrometer and analysed by exploding with air in a Hempel pipette, with the following results:

	Expt. I.	Expt. II.
Gas taken	11·22 c.c.	11·4 c.c.
Air added	50·28	58·0
Contraction	16·0	16·4
Composition of gas { hydrogen	10·7	10·9
Composition of gas { residual gas	0·52	0·5

As the gas for analysis was all collected in the space of about 10 minutes, and as, at the close of the experiment, on allowing the apparatus to cool in a current of ammonia for an hour or more after driving out the hydrogen from the apparatus, practically the whole of the gas was absorbed by the acid in the nitrometer, the residual gas above-mentioned can scarcely be nitrogen derived from air present in the apparatus, but must be due to the dissociation of ammonia. It seems probable that on passing ammonia over reduced iron at a temperature rather above 400°, ammonia is dissociated, the nitrogen at the moment of its liberation combining with the iron. A certain small proportion, however, will escape combination thus, and pass on uncombined along with the hydrogen. Ramsay and Young (*loc. cit.*) give the temperature at which ammonia begins to dissociate under the most favourable circumstances as a little below 500°. The above experiments tend to show that dissociation begins at a lower temperature under the conditions described. In confirmation of another of Ramsay and Young's results, it may be mentioned that on heating ammonia in a sealed tube to a temperature approaching redness no decomposition ensued.

(c) *Preparation of Iron Nitride from Iron Amalgam.*—Recent investigations have shown that iron and other metals, when liberated from their amalgams, have specially energetic properties (Guntz, *Compt. rend.*, 1892, **114**, 115; Maquenne, *ibid.*, 25, 220). Accordingly, some iron amalgam was prepared by Joule's method (*Mem. Manchester, Lit. and Phil. Soc.*, 1865, [iii], **2**, 115). A saturated solution of ferrous sulphate was electrolysed by a weak current, a bundle of iron wire constituting one electrode, the other being a piece of platinum foil attached to a stout platinum wire, which was inserted into a glass tube filled with mercury, by which connection was made with the battery. The platinum foil dipped under mercury contained in a small, deep porcelain dish. On passing the current, iron amalgam is formed round the platinum. It is important to use a weak current, or the iron is deposited in a powdery state, and does not amalgamate with the mercury. The excess of mercury is squeezed from the

amalgam, which is obtained of a buttery consistency, and contains about 10 per cent. of iron as determined by ignition. Joule's soft amalgam contained 11·8 per cent. of iron. This amalgam rapidly blackens in air, even when carefully washed free from acid; it blackens also under water. On drying some of this amalgam and heating in ammonia, the mercury was driven off and iron nitride gradually formed from the porous iron left. The latter, however, seems to offer no advantage over ordinary reduced iron for the preparation of the nitride. Doubtless this is to be expected from the character of the reaction, there being always the same tendencies to break up the nitride formed. A determination of nitrogen in the substance formed by long-continued action of ammonia gave 9·16 per cent., showing that only partial conversion had taken place. That this percentage was taken up by degrees was evident from the fact that after the mercury was expelled the weight gradually increased on continuing the action of ammonia. Also the iron, obtained after driving off the mercury, was readily attracted by a weak magnet, which is not the case with iron nitride. The percentage of nitrogen was found to vary somewhat between the more and less finely divided portions of substance.

Before leaving the subject of the preparation of iron nitride, it should be mentioned that Stahlschmidt unsuccessfully attempted to make this compound by heating iron and nitrogen together, and also by passing a mixture of nitrogen and hydrogen over heated ferrous oxide. His results are therefore at variance with those of Briegleb and Geuther and of Rogstadius (*loc. cit.*).

This point was investigated in the present research as follows. About 7·5 grams of reduced iron were sealed up in a glass tube 30 cm. long and 2 cm. diam. in an atmosphere of nitrogen. After heating at 180° for 5 hours, and again at 330° for 8 hours, the tube was opened under mercury. There was no indication that absorption had taken place. On resealing and heating at 420° for 4 hours, and at 470° for 6 hours, no indication of absorption was noted on opening under mercury. It may be concluded, therefore, that under these conditions iron and nitrogen do not combine.

No attempt was made to obtain iron nitride by electrolysis, as the experiments of Classen (*Quantitative chemische Analyse durch Elektrolyse*, 1886, p. 55), confirmed by laboratory experience, show that pure iron is obtained on electrolysing a solution of ferrous ammonium oxalate.

Analysis of Iron Nitride.

That all the nitrogen is converted into ammonia on solution, and that the substance consists solely of iron and nitrogen, was proved by

analysis of a sample which was used for a determination of the heat of formation. In this case, the compound was dissolved in sulphuric acid, the iron oxidised by nitric acid, precipitated by ammonium hydroxide, and the ferric hydroxide washed, ignited, and weighed. In this case, the solution in the calorimeter was diluted to one litre, and 500 c.c. taken for analysis.

0·6625 gave 0·8466 Fe_2O_3. Fe = 89·4 per cent.

The nitrogen was determined by distilling the nitride with caustic soda, absorbing the evolved ammonia in hydrochloric acid, and estimating as platinum salt. Two determinations were made:

0·1714 gave 0·2836 $(NH_4)_2PtCl_6$. N = 10·46 per cent.
0·3126 „ 0·5791 $(NH_4)_2PtCl_6$. N = 10·5 „
The composition therefore is Fe = 89·4; N = 10·48 (mean). Total = 99·88

Although this sample still contained a small quantity of free iron, the analysis shows that the nitride most probably dissolved according to the following equation:

$$2Fe_2N + 6H_2SO_4 = 4FeSO_4 + 2(NH_4)HSO_4 + H_2.$$

This is rendered certain by further experiments.

Another sample was analysed in the following manner. A weighed quantity was dissolved in hydrochloric acid, evaporated on a water-bath with platinic chloride to almost complete dryness, and taken up with absolute alcohol. On filtering and washing with absolute alcohol, the ammonium platinichloride can be obtained free from traces of iron, if care be taken to leave a trace of free hydrochloric acid in the evaporating basin before adding alcohol. This method was used throughout as allowing of greater accuracy with small quantities than a method involving distillation. The following result was obtained:

0·2020 gave 0·3537 $(NH_4)_2PtCl_6$. N = 11·07 per cent.
Fe_2N requires N = 11·11 per cent.

The percentage of platinum found after ignition of the double salt was 43·77, the calculated percentage for the ammonium salt being 43·79. This result shows that only ammonium compounds are formed when the nitride is dissolved in acids.

This conclusion is confirmed by a determination of the hydrogen evolved when the nitride is dissolved in sulphuric acid. The determination was made by enclosing a weighed portion of the substance in a small tube and quickly inserting under a gas measuring tube standing in a small glass trough. Both tube and trough were filled with dilute sulphuric acid. The gas was prevented from escaping from beneath the measuring tube by means of a funnel. Correction was made for

the amount of air enclosed in the small tube containing the substance; it amounted to 0·3 c.c.

0·275 gave 23·1 c.c. hydrogen (N.T.P.). The calculated amount is 24·4 c.c. assuming the nitride to dissolve according to the equation:

$$2Fe_2N + 6H_2SO_4 = 4FeSO_4 + 2(NH_4)HSO_4 + H_2.$$

Allowing for the fact that a little hydrogen will dissolve, these figures are in sufficient agreement with the equation, and show plainly that no hydrogen enters into the composition of the nitride and that no nitrogen compounds other than ammonium salts are formed by treatment with acid.

The iron in the same sample was determined. (a) By treatment with nitric acid and subsequent ignition:*

0·4215 gave 0·5325 Fe_2O_3. Fe = 88·43; calc. 88·88 per cent.

(b) The nitride was dissolved in sulphuric acid and the solution diluted to 250 c.c. and titrated with potassium permanganate (1 c.c. = 5·505 mgms. Fe), after reduction of any oxidised iron by means of zinc:

0·4833 required 15·6 × 5 c.c. $KMnO_4$ (mean of 3 titrations). Fe = 88·82.
0·5185 „ 16·6 × 5 c.c. $KMnO_4$ „ „ Fe = 88·1.
Fe_2N requires Fe = 88·88 per cent.

No percentages of nitrogen above 11·1 could be obtained, whilst any percentage below that could be got according to the time during which the iron had been exposed to the current of ammonia.

These results are fully in agreement with those obtained by Stahlschmidt, and confirm his conclusion that only one iron nitride exists, and that it has the composition expressed by the formula Fe_2N.

Physical Properties of Iron Nitride. Appearance and Magnetic Qualities.

Iron nitride, prepared as above described, is a grey powder, of a rather duller tone than reduced iron. One of the difficulties in working with this substance is that it is impossible from its appearance alone to tell whether it is even approximately pure. The powder is gritty, and the particles under the microscope have a vitreous appear-

* Satisfactory results could not be obtained by simply igniting in air, and weighing the oxide of iron formed owing to the varying percentages of magnetic oxide produced. This source of error seems to have escaped notice by Stahlschmidt, who determined his iron by simple ignition. By heating with nitric acid and decomposing the resulting nitrate, better, but not entirely satisfactory, results are obtained. As it is the practice in some commercial analytical laboratories to incinerate filter papers together with an adhering precipitate of iron oxide, whereby iron is reduced and subsequently oxidised largely to magnetic oxide, this source of error deserves mention.

ance differing from reduced iron, which appears powdery. Although not attracted by a strong bar magnet, a moderately strong electromagnet readily attracts it. The magnetic property of iron is therefore still apparent, even when this element is combined with nitrogen.

Specific Gravity.—This was determined by means of the specific gravity bottle, using benzene and water as liquids for comparison. The quantity of iron nitride available for the determination was rather small, being about 0·5 gram, so that two results obtained with benzene varied from 6·55 to 6·065.

In each case, concordant weighings only were taken. Using water as the liquid for comparison, the value 6·25 was obtained. A determination made at the same time of the specific gravity of reduced iron gave the value 7·89. The above value for the sp. gr. of iron nitride is rather higher than the number 5 given by Despretz for the nitride described as a white, brittle mass.

It is of interest to compare the following sp. gr., taking in all cases the highest value recorded :

Reduced iron.....	7·89	Magnetic oxide, Fe_3O_4 ...	5·2
Iron nitride, Fe_2N	6·25	Ferric oxide, Fe_2O_3	5·17

Taking the molecule of iron to be diatomic, we get the following values for the atomic volumes :

Iron	7·1	O in Fe_3O_4	5·8
Nitrogen in Fe_2N.....	5·9	O in Fe_2O_3	5·6

Chemical Reactions of Iron Nitride.

Oxidation.—Air or oxygen dried by sulphuric acid was passed over the nitride contained in a boat placed in a L. Meyer constant temperature furnace. The escaping gas was passed into potassium iodide. On heating to 120°, a slight liberation of iodine took place (about 5 milligrams), and there was a gain in weight of about 3 milligrams on half a gram of the substance. Oxidation became visible at 200°, brown ferric oxide being formed; there was no increase, however, in the amount of iodine liberated. The nitrogen therefore appears not to suffer appreciable oxidation under these conditions, the slight liberation of iodine being possibly due to nitric peroxide produced by the oxidation of a trace of ammonia occluded in the nitride.

Chlorine.—The action of chlorine was examined by placing some of the nitride in a boat enclosed in a tube, and passing chlorine over after displacing the air by carbon dioxide. Any nitrogen given off could then be recognised by passing the gases through strong potash solution contained in an ordinary nitrogen measuring tube. The nitride takes fire in chlorine on slightly warming, or sometimes spon-

taneously, ferric chloride being produced and nitrogen evolved. There is no evidence of the formation of nitrogen chloride, said to be produced when chromium nitride is similarly treated.

Bromine.—Bromine attacks the nitride only slowly, even on warming, and as ammonium bromide was always found in solution after action had taken place, it is probable that the reaction is chiefly brought about by the trace of hydrobromic acid contained in the bromine.

Iodine.—An ethereal solution of iodine has no action on iron nitride.

Hydrochloric and Sulphuric Acids.—The action of these acids in the diluted condition has already been described, namely, the nitride is dissolved, ferrous and ammonium salts being formed, and hydrogen liberated.

Nitric Acid.—This acid, even if strong, acts only slowly. Its action was not exhaustively studied, as it must vary much according to the strength. The main reaction, doubtless, is the formation of ammonium nitrate and the products of the action of nitric acid on iron, nitrous or nitric oxides being formed according to the strength of the acid. No great evolution of nitrogen peroxide takes place on warming with moderately concentrated nitric acid.

Hydrogen Chloride.—It is interesting to note that, whilst hydrochloric acid rapidly attacks the nitride in the cold, gaseous hydrogen chloride only begins to attack it at about 220°, the action becoming rapid at 350°, complete conversion into ferrous chloride and ammonium chloride taking place.

Nitric Oxide.—The action of nitric oxide was examined in order to compare the temperature of oxidation with that at which free oxygen begins to act on the substance, and also to see whether the nitrogen which would be evolved in such a reaction differed in its properties from ordinary nitrogen.

It seemed possible that the following reaction might take place:

$$Fe_2N + 2NO = 2FeO + N_3.$$

In view of the opinion put forward by Berthelot and others that argon may be condensed nitrogen of the formula N_3, it became of interest to examine the gas given off in the experiment to see whether such a condensation occurred under these conditions.

Oxidation began at about the same temperature as in oxygen, namely, at about 120°, becoming rapid at 170°; the gas evolved was collected, and, after removal of the nitric oxide by ferrous sulphate solution, was sparked with oxygen over potash, being practically all absorbed. It may be concluded therefore that the gas produced when nitric oxide acts upon iron nitride is ordinary nitrogen.

Action of Carbon Monoxide.—On heating the nitride to a tempera-

ture approaching redness in a current of carefully purified carbon monoxide, freed from moisture, oxygen, and carbon dioxide by passing successively through strong sulphuric acid, red hot copper gauze, potash, and strong sulphuric acid, a slight loss of weight took place and the substance darkened somewhat in colour. On passing the gas into lime water, a precipitate of calcium carbonate showed that carbon dioxide had been formed. This may either result from the reduction of a trace of oxide in the substance or from the decomposition of the carbon monoxide, the darkening above-mentioned being due to deposition of carbon as in the experiments of Lowthian Bell. On passing the escaping carbon monoxide into potash solution, no cyanogen compounds could be detected in the latter, so that the nitrogen does not appear to combine with carbon under these conditions. Possibly some iron cyanide may be formed, but this was not looked for at the time.

Carbon Dioxide.—It was thought at first that the temperature of decomposition of the nitride might be found by heating in carbon dioxide. Accordingly, some of the compound was heated in this gas in a tube surrounded by vapour of mercury, and afterwards by that of boiling sulphur. At the temperature of the latter, 448°, the nitride was oxidised, as could be judged by the change in appearance and the increase in weight.

In another experiment, the compound was strongly heated in a boat placed in a tube through which a current of carbon dioxide was passed, the escaping gas being collected over potash. It was found to consist chiefly of carbon monoxide, some nitrogen, however, being left after absorbing the carbon monoxide with ammoniacal copper solution. No definite equation can be given for this reaction, as the increase in weight observed in the nitride may be due partly to deposition of carbon as well as to oxidation. Assuming, however, magnetic oxide to be formed on oxidation, the ratio between the nitrogen and carbon monoxide should be rather more than 1 to 5. Out of 17·8 c.c. taken for analysis, 3·4 were not absorbed by copper solution, giving approximately this ratio. The temperature at which nitrogen is given off in this way was roughly determined by noting the behaviour of salts of known melting point placed in small pieces of platinum foil on the heated tube. As the temperature was above the melting point of lead chloride and about that of calcium chloride, 530° may be taken to represent the temperature at which iron nitride is oxidised by carbon dioxide. It is possible that the nitride used contained small quantities of free iron, but as more than 10 per cent. of nitrogen was present and as any finely divided iron present is rapidly oxidised in air, the amount of free metal present could be but small.

Action of Hydrogen Sulphide.—On heating with hydrogen sulphide,

increase in weight took place, and a strong smell of ammonia was noticed in the soda-lime used to absorb the excess of hydrogen sulphide at the end of the tube.

The hydrogen sulphide was obtained pure by heating a solution of magnesium hydrosulphide. The substance left in the boat after heating in hydrogen sulphide contained iron sulphide, as it evolved hydrogen sulphide on treatment with an acid. The reaction taking place when hydrogen sulphide is heated with iron nitride is evidently expressed by the equation:

$$2Fe_2N + 6H_2S = 4FeS + 2NH_4HS + H_2.$$

The temperature at which this reaction occurs was approximately ascertained by heating the nitride in a current of hydrogen sulphide in a test-tube immersed in a bath of sulphuric acid. The gas, after passing over the nitride, was conducted into a neutral solution of ferrous sulphate. As soon as ammonia was formed, ferrous sulphide was precipitated. This took place at about 200°. Hydrogen sulphide alone was found not to precipitate neutral ferrous sulphate.

Action of Steam.—When the nitride was heated in a current of steam, kept at 100° by a bath of boiling water, a very slight evolution of ammonia was noticed, the litmus paper being slowly but continuously turned blue.

Behaviour with Carbon.—On heating iron nitride with carefully purified sugar charcoal (freed from hydrogen by chlorine) in a tube closed at one end and passing any evolved gas into potash, no reaction for cyanides could be obtained in the latter. The nitrogen in the nitride appears therefore to have no tendency to combine with carbon either in the free state or as carbon monoxide. In presence of sodium, however, the two elements combine and sodium cyanide is formed. On heating a small amount of the nitride with pure charcoal and a small piece of freshly cut sodium, a reaction takes place, and on dissolving out in water a strong Prussian blue reaction is given on adding a mixture of ferrous and ferric salts and acidifying. The reaction was not given after heating the charcoal and sodium alone.

Copper Sulphate.—Neutral copper sulphate solution is without action on iron nitride; on slight acidification, copper is precipitated, the nitrogen going into solution as ammonia.

Phenol.—In order to compare the action of phenol, as a typical substance of slightly acid nature, with the behaviour of ordinary mineral acids, the nitride was heated with phenol in a sealed tube at 220°. No appreciable change took place, no pressure was created in the tube, and the substance after extracting with ether and washing was unaltered in appearance. The weight of nitride obtained after the treatment differed only slightly from the weight taken for experi-

ment. It may be concluded therefore that phenol and compounds of a like nature are without action on iron nitride.

Ethyl Iodide.—In order to ascertain whether amines would be produced by the action of ethyl iodide on the nitride, the two compounds were heated together in a sealed tube. Up to 150°, no action took place, judging by the absence of pressure in the tube, on opening after it had been exposed to that temperature. After heating for some time to 200—230°, considerable action took place, blackish, iodine-like crystals being formed and much gas produced. This gas was collected by breaking the end of the tube under a piece of indiarubber tubing communicating with a laboratory tube. On analysis of the gas in the Hempel apparatus, it was found to consist of olefines to the amount of one-third and a slight trace of paraffins, in addition to the air previously in the tube.

On boiling the crystals above mentioned with caustic soda, ammonia was evolved and iron hydroxide formed. On distilling with caustic soda, collecting the escaping gas in hydrochloric acid, and evaporating this solution with platinic chloride, a platinum salt was obtained which on ignition gave Pt = 44·9 per cent. $(NH_4)_2PtCl_6$ requiring Pt = 43·7. No amines are therefore formed in this reaction, which is probably as follows:

$$2Fe_2N + 10C_2H_5I = 2NH_4I + 10C_2H_4 + 4FeI_2 + H_2.$$

Action of Hydrogen Peroxide in Presence of Acid.—It was thought of interest to study the simultaneous action of an acid and an oxidising agent on iron nitride, in order to see whether in such a case the nitrogen would be wholly converted into ammonia, become partially oxidised to hydroxylamine, or partially escape in the free state. Weighed quantities of nitride, containing 9 to 10 per cent. of nitrogen, were therefore treated with a mixture of hydrogen peroxide and sulphuric acid, excess of hydrogen peroxide being used. The nitrogen was determined in solution after dissolving, by distilling with caustic soda, collecting the evolved gas in hydrochloric acid, and determining the ammonia as platinichloride.

The nitrogen was also determined in a similar sample dissolved in acid without hydrogen peroxide. The results obtained show conclusively that most, at any rate, of the nitrogen is not oxidised. In one comparison, the percentages of nitrogen found in the two experiments were almost exactly the same, namely, 8·82 without and 8·73 with hydrogen peroxide. Analysis of the gas evolved on solution of iron nitride in a mixture of sulphuric acid and hydrogen peroxide showed that it consisted chiefly of hydrogen and oxygen. The small amount of residual gas was not enough to lead to the conclusion that nitrogen had escaped conversion into ammonia.

Temperature of Decomposition of Iron Nitride.—A minimum value for this was obtained by heating the substance in a current of nitrogen. Up to the temperature of boiling sulphur, 448°, no change in weight took place. A very slight loss occurred at a temperature approaching dull redness. The temperature of decomposition must therefore certainly be above 600°.

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XXX.—*The Heat of Formation and Constitution of Iron Nitride.*

By GILBERT JOHN FOWLER, M.Sc. (Vict.), and PHILIP JOSEPH HARTOG, B.Sc. (Lond. and Vict.).

WHEN iron nitride is dissolved in dilute acids, it is decomposed and yields salts of iron and of ammonium, hydrogen being evolved at the same time. These reactions offer a convenient method for the determination of the heat of formation of the nitride. Dilute sulphuric acid was found more suitable than hydrochloric acid for the purpose. The equation corresponding to the reaction is as follows (Fowler, this vol., p. 292):

$$2Fe_2N + 6H_2SO_4,aq = 4Fe_2SO_4,aq + 2NH_4HSO_4,aq + H_2.$$

Experimental Details.

The acid used contained 49 grams of H_2SO_4 to the litre. Six hundred grams were introduced into a platinum calorimeter provided with a cover and supported on three corks inside a Berthelot water-jacket. The liquid was agitated by a platinum screw-stirrer revolving about four times a second, and a regular current of nitrogen was led through the liquid to prevent any oxidation of the ferrous sulphate formed. The thermometer used was one by Baudin (No. 12770), graduated to fiftieths of a degree.

After observing the thermometer during a preliminary period until the rate of change was steady, the iron nitride was introduced, and readings taken every minute until the rate of change was again steady. The reaction is a somewhat slow one; in the three experiments made, the time needed for complete solution was 31, 44, and 50 minutes respectively. The correction was calculated graphically by the Regnault-Pfaundler method, and the agreement of the three results shows that the determinations are satisfactory in this respect.

The solution yielded only the faintest possible coloration with potassium thiocyanate at the conclusion of the experiments.

The specific heat of the final solution was taken to be equal to that of the solution of sulphuric acid used; this involves no appreciable error. One hundred grams of the solution, according to Kolb (Landolt and Börnstein, *Tabellen*, 1883, p. 140), contain 4·8 of H_2SO_4; hence its composition is $H_2SO_4,108H_2O$. The specific heat was calculated by the formula of Mathias, from Thomsen's experiments (*Journ. de Physique*, 1889, [ii], 8, 204), $c=(a+n)/(b+n)$ where $a=2{\cdot}407$, $b=7{\cdot}074$ and $n=108$. This gives $c=0{\cdot}9603$ and the equivalent in water of 600 grams of acid $=576{\cdot}1$.

A further correction had to be made for a small amount of iron existing in the nitride. The specimen used contained 94·22 per cent. of Fe_2N and 5·78 of Fe. The heat of solution of iron in dilute sulphuric acid was taken from Thomsen's determinations as 24·84 Cal. for 56 grams.

The following are the details of the experiments:

Water equivalent of calorimeter and contents (including acid, stirrer, part of thermometer immersed, &c.).	Weight of substance dissolved, in grams.	Rise of temperature.	Cooling correction.	Total number of Calories evolved.	Calories evolved by the solution of free iron in the nitride.	Thermal value of reaction in Calories.*
588·5	0·842	0·9644	−0·0605	0·5320	0·0216	81·06
588·5	0·841	0·8888	+0·0274	0·5392	0·0216	82·30
588·5	1·325	1·3525	+0·0741	0·8396	0·0340	81·31

The mean for the three determinations is 81·56.

* Account has been taken in the calculation of the fact that the substance only contains 94·22 per cent. of nitride and 5·78 per cent. of iron.

Calculation of the Heat of Formation of Iron Nitride.

If we start from a given initial system and pass to a given final system by two different cycles of transformations, we may assume that the total heat evolved is in both cases the same.

We take as the initial system $2Fe+N+6H+3S+12O+aq.$

„ „ final system $2FeSO_4,aq.,+NH_4HSO_4,aq.+H.$

Cycle I.

			Thermal value of reaction.
Fe_2+N	=	Fe_2N	x
$3(H_2+S+O_4)+aq.$	=	$3H_2SO_4,aq.$	$3a_1$
$Fe_2N+3H_2SO_4,aq.$	=	$2FeSO_4,aq.+NH_4HSO_4,aq.+H$	81·56

* If Marignac's determinations of specific heats are used $c=0{\cdot}9578$.

Cycle II.		Thermal value of reaction.
$2Fe + 2S + 8O + aq.$	$= 2FeSO_4,aq.$	$2a_2$
$N + 6H + S + 4O + aq.$	$= (NH_4HSO_4,aq.) + H$	a_3
$FeSO_4,aq. + NH_4HSO_4,aq.$	$= FeSO_4,aq. + NH_4HSO_4,aq.$	0*

We have the equation $x = -3a_1 + 2a_2 + a_3 - 81{\cdot}56$.

According to Berthelot, $a_1 = 210{\cdot}1$ Cal., $a_2 = 234{\cdot}9$ Cal., $a_3 = 245{\cdot}1$ Cal.

According to Thomsen, $a_1 = 210{\cdot}77$ Cal., $a_2 = 235{\cdot}6$ Cal.

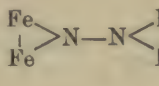
If we adopt all Berthelot's values, we find $x = 3{\cdot}04$ Cal.

If we adopt Thomsen's values for a_1 and a_2, and Berthelot's for a_3, $x = 2{\cdot}43$ Cal.

It would require careful investigation of the data on which Thomsen's values are based to see if the latter method of calculation is justifiable and does not involve the use of two different values for the same thermal constant.† We prefer to adopt the number 3·04 Cal.

The heat of formation of iron nitride being so small, we might expect it to behave towards reagents in much the same way as free iron, yet although it is attacked by chlorine, as one of us has shown (Fowler, *loc. cit.*), neither bromine nor iodine has any action on it. This fact is remarkable.

It is impossible at present to determine the molecular weight of iron nitride. The formula Fe_2N is obviously irreconcilable with received theories unless we make the gratuitous assumption that 1 atom of iron is tervalent and the other bivalent, the nitrogen being quinquevalent. It seems more probable that the molecular formula is Fe_4N_2, the constitution being:



The thermochemical apparatus used belongs to the Royal Society, and was bought from a grant made to one of the authors for other calorimetrical work.

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* The heat of solution of ferrous sulphate first in water and then in a solution of ammonium sulphate was determined, and the difference was found to be 0·05 Cal. With a solution of hydrogen ammonium sulphate, the difference would probably have been even less, as ferrous sulphate does not form a double salt with this compound. The thermal value of the reaction has therefore been neglected in the calculations, as the error committed is less than the inevitable error of experiment.

† The data quoted are taken from Berthelot's *Thermochimie*, 1897.

XXXI.—*The Preparation of Iodic Acid.*

By Alexander Scott and William Arbuckle.

In a note on the preparation of iodic acid appended to the first part of his "*Nouvelles Recherches*," Stas states that the yield of iodic acid obtainable by oxidising iodine by means of nitric acid has been much exaggerated, and that the quantity of pure iodic acid obtained does not represent a quarter of the iodine employed. If this statement is correct, the question arises, What becomes of the rest of the iodine? Experiments were therefore made to test its truth. Into a round bottomed flask with a very long neck, 100 grams of iodine were placed, and boiled gently with nitric acid (sp. gr. 1·5) repeatedly renewed, the more or less spent acid being removed each morning and replaced with strong acid. In order to oxidise all the iodine this had to be continued for about ten days of eight hours each. By careful regulation of the flame so as to minimise the loss of iodine due to its being carried off with the steam and oxides of nitrogen, 102 grams of iodic acid were obtained, that is, about 74 per cent. of the iodine employed had been obtained as iodic acid.

As this method is very tedious and, even as carried out above, wasteful both as regards iodine and nitric acid, other forms of ap paratus were tried with varying degrees of success.

The first apparatus employed was a Soxhlet's fat extraction apparatus, all the joints being glass to glass, the iodine being treated as if it had to be extracted, and the fuming nitric acid placed in the flask. In the first experiment, 20 grams of iodine and 150 c.c. of fuming nitric acid were employed, and 26 grams of iodic acid were obtained (93 per cent.). Next 50 grams of iodine and 200 c.c. of nitric acid were employed and 60 grams of iodic acid obtained (86 per cent.). The action was rapid, the only, but very serious, objection to this form of apparatus being the liability of the narrow siphon tube to become choked by the deposition in it of crystals of iodic acid. When this occurs, the operation must of course be stopped.

By varying the diameter of the tubes, some improvements were effected, but, as much simpler and more efficient forms of apparatus have been devised, it is unnecessary to describe these intermediate forms.

The best form of apparatus is a flask like that recommended for the preparation of pure hydrobromic acid (Trans., 1900, 77, 649), but having the tube *C* sealed to a reflux condenser; through *B* a tube is fitted (by means of a small piece of rubber tubing) by which a current of oxygen may be passed through the boiling acid, the point

of the tube reaching almost to the bottom of the flask. With this apparatus, iodine *in fine powder* boiled with ten to twelve times its weight of nitric acid (sp. gr. 1·5) is completely converted into iodic acid in from twenty minutes to half an hour.

The other and more easily obtainable form of apparatus is a long necked flask such as was employed in the first experiment. In the neck of this flask is inserted a condenser of the well-known form made of quill tubing bent so as to form a long double U-tube and a brisk current of cold water is kept circulating through it. A current of oxygen should be passed through the acid during the oxidation, care being taken that the tube very nearly touches the bottom of the flask, otherwise very violent bumping takes place owing to the heavy deposit of iodic acid crystals. With this apparatus, to get the reaction to go completely and quickly, a greater proportion of nitric acid is required. Moreover, it does not work well with larger quantities than 20 grams of iodine at a time, as the following results show: 20 grams of iodine gave 27 grams of iodic acid in 25 minutes, but from 40 grams of iodine only 49 grams were obtained after oxidation for an hour. A current of air is also of assistance if oxygen is not available, but either a somewhat larger proportion of nitric acid or a longer time must be employed to complete the oxidation.

Experiments in which the iodine was volatilised in the current of oxygen and passed as vapour into the boiling nitric acid were tried, but without much success.

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XXXII.—*The Reaction between Ethyl Alcohol and Hydrochloric Acid.*

By THOMAS SLATER PRICE, D.Sc. (late 1851 Exhibition Scholar).

VARIOUS chemists have studied the velocity of formation of esters and the equilibrium attained; among them may be mentioned Berthelot and Péan de St. Gilles (*Ann. Chim. Phys.*, 1862, [iii], **65**, 385; **66**, 5; 1863, **68**, 225); Guldberg and Waage (*J. pr. Chem.*, 1879, [ii], **19**, 69); van't Hoff (*Ber.*, 1877, **10**, 669); Villiers (*Ann. Chim. Phys.*, 1880, [v], **21**, 72); Cain (*Zeit. physikal. Chem.*, 1898, **12**, 751); Petersen (*ibid.*, 1895, **16**, 385); Tafel (*ibid.*, 1896, **19**, 592); Knoblauch (*ibid.*, 1897, **22**, 268); and Goldschmidt (*Ber.*, 1895, **28**, 3218; 1896, **29**, 2208; *Zeit. physikal. Chem.*, 1899, **31**, 343).

Berthelot's attempt to apply a mathematical formula to the velocity of reaction was not quite successful, as was also the case with the application of the law of mass action by Guldberg and Waage.

Van't Hoff attacked the question independently of Guldberg and Waage, and on the assumption that the velocity of reaction was proportional to the product of the active quantities of the substances present, he deduced the ordinary velocity equation for a reversible reaction, namely:

$$\frac{dx}{d\theta} = k_1(A-x)(B-x) - k_2(C+x)(D+x) \quad \ldots\ldots\ldots\ldots (1),$$

where A, B, C, and D are the concentrations * of the alcohol, acid, ester, and water respectively, at the commencement of the reaction; x is the quantity of ester formed after the time θ, and k_1 and k_2 are velocity constants.

This gives for the state of equilibrium:

$$\frac{dx}{d\theta} = k_1(A-\xi)(B-\xi) - k_2(C+\xi)(D+\xi) = 0$$

$$\therefore \quad \frac{(A-\xi)(B-\xi)}{(C+\xi)(D+\xi)} = \frac{k_2}{k_1} = a \quad \ldots\ldots\ldots\ldots\ldots\ldots (2),$$

where ξ = quantity of ester which has been formed in addition to the amount started with.

On applying this equation to the experiments of Berthelot, the agreement between theory and experiment was fairly satisfactory.

Knoblauch (*loc. cit.*) finally proved the complete applicability of this velocity equation in the case of the action of acetic acid on ethyl alcohol. Both the direct and reverse reactions were studied, and the results agreed with theory.

The reaction is, however, always more complicated than is represented by the first equation given above, as other factors have to be taken into account, as, for example, the possible catalytic effect of the hydrogen ions of the acid. Knoblauch got rid of this difficulty by adding a known amount of a strong mineral acid (hydrochloric acid), thus keeping the number of the hydrogen ions constant, as the dissociation of the acetic acid is small, and would be still further reduced by the presence of the hydrochloric acid. The latter, at 25°, does not take any part in the reaction, and simply acts as a catalyser.

* The concentration is assumed to be proportional to the active quantities. This is only strictly true in dilute solution, compare p. 310.

The Case of Equilibrium.

Berthelot and St. Gilles have shown that in the case of organic acids the point of equilibrium is *independent of the temperature*. The value of $1/\alpha = k_1/k_2$ which they found for ethyl alcohol and acetic acid was 4. Knoblauch found for the same 2·74, but his experiments were carried out in aqueous solution, whereas Berthelot and St. Gilles obtained their results by mixing the pure acid and alcohol. He does not give any explanation of this difference, but in a footnote merely says "Durch den Zusatz der Chlorwasserstoffsäure nimmt also k_1/k_2 einen kleineren Wert an."

Goldschmidt has further studied the same reaction and obtained a similar result, using picric acid as a catalyser, the value of the constant $(1/\alpha)$ increasing with increase of concentration of the picric acid. He also made an experiment with a normal solution of hydrochloric acid (Knoblauch used acid of a strength less than normal) and found the value 3·46.

FIG. 1.



In the case of the equilibrium attained when mineral acids act on the alcohols, the effect of temperature is very different from the above. Villiers found in the case of the action of hydrochloric, hydrobromic, and hydriodic acids on alcohol, that the amount of ester formed increases with the temperature, that is, α diminishes as the temperature rises. It can also be shown from his results that α is variable.

Cain applied Guldberg and Waage's law to the equilibrium attained in the reaction between hydrochloric acid and ethyl alcohol, and found that the values of $1/\alpha$ so obtained varied between 7·49 and 8·80.

As the results obtained by former investigators for the equilibrium constant between ethyl alcohol and hydrochloric acid varied so much, it was necessary for me to make some independent determinations.

The method of preparing and storing the reaction mixture was similar to that of Cain (*loc. cit.*), dry hydrogen chloride being passed into the anhydrous alcohol. Drying tubes were always interposed between the stock solution and the outside air.

The reaction tubes were of the shape shown in the diagram. The reservoir *A* had a volume of from 2 to 3 c.c., *B* and *C* were capillary tubes with constrictions at *b* and *c* to facilitate sealing off. The tubes were all thoroughly cleaned with chromic acid mixture, and then steamed out for about 15 minutes each tube. The method of filling from the store flask was as follows. The end *C* was put down into the reaction mixture (compare Cain, *loc. cit.*) and the solution forced

up into *A* until the reservoir was nearly full. The tube was then taken from the flask and sealed off at *b*; this left *C* full and *A* nearly full of the solution. It was allowed to stand until the glass at *b* was cool, then inverted and immersed in broken ice, and after an interval, about half the solution which remained in the capillary tube *C* was drawn into the reservoir *A* The tube was then taken out of the ice and *A* warmed with the hand until the solution in the capillary was driven past the constriction *c*, where it was then sealed off. By this means any of the solution which had come in contact with the air and could thus have absorbed moisture was rejected, as diffusion through the capillary would take place very slowly. Thus only a reaction mixture which was free from moisture came into use.

The amount of solution in each tube was measured by weighing it before and after filling. The strength of any solution was then found by titrating the contents of any one tube with standard baryta solution. The filled tubes were kept at 0° (at which temperature the reaction does not proceed) until required. Aqueous solutions were prepared by running some of the anhydrous solution into a weighed quantity of cold water. The accuracy of this method is shown by the following figures:

61·2879 grams of a solution of 33 equivalents of hydrogen chloride in 100 equivalents of alcohol were mixed with 20·4669 grams of water. The composition of the mixture (in equivalents) is then calculated to be $100C_2H_5{\cdot}OH : 33{\cdot}00HCl : 107{\cdot}66H_2O$, and in 1 gram of the mixture there should be 0·1554 gram HCl. The HCl found was 0·1553 gram.

A constant temperature was obtained by means of thermostats of the form described in Ostwald's "Hand- und Hilfs-buch," pp. 61—62. Experiments were carried out at 77°, 99°, and 129·5°.

In making a determination of the equilibrium, there are several factors to be taken into account. Berthelot and St. Gilles have shown that pressure has very little influence on the equilibrium, an increase of pressure of 80 to 90 atmospheres scarcely affecting the result. On the other hand, the volume of the space in which the reaction takes place is of great importance, especially at high temperatures, when the constituents can assume the vapour phase, the esterification then tending to become more complete. This effect of volume is clearly shown by the results recorded on p. 307 in which the mixture used contained 100 alcohol : 31·83HCl (equivalents).

Thus, when the tube is two-thirds or more full, the value of α remains constant; otherwise it increases as the volume occupied by the mixture decreases. In all determinations, care was therefore taken that the tubes were about three-quarters full.

In order to be certain that equilibrium had been reached, separate

Temp. = 99°. Time of heating = 5 days.

Weight of mixture in tube.	Vol. of tube occupied.	α (equilib. const.).
1·0963 grams	One-third	0·197
1·6994 ,,	One-half	0·184
2·2995 ,,	Two-thirds	0·179
2·8069 ,,	Four-fifths	0·177

tubes were heated for different lengths of time in order to see if the titre of the acid remained constant. To show the measure of accuracy obtained, one experiment is given in detail :

Weight of mixture.	Time of heating.	Titre in c.c. baryta.	Titre for 1 gram.
2·4620 grams	96 hours	6·20	2·52
1·9837 ,,	72 ,,	5·04	2·54
2·0298 ,,	72 ,,	5·02	2·47
1·9627 ,,	144 ,,	5·00	2·55

In measuring the strength of the solution, $100C_2H_5OH : 33HCl$ (equivalents), the following were the figures obtained :

Weight of mixture.	Titre in c.c. baryta.	Titre for 1 gram.
2·1289 grams	78·01	36·64
2·0499 ,,	75·20	36·69
2·4794 ,,	90·85	36·66
2·3420 ,,	86·15	36·78

The accuracy of the measurements is thus all that could be desired.

The following tables give the results of different experiments. The first three columns give the composition of the mixture started with ; the next four give the composition when equilibrium was reached, and the last column gives the values of α so obtained. The compositions are all expressed in equivalents :

Equilibrium at 99°.

C_2H_5·OH.	HCl.	H_2O.	C_2H_5·OH.	HCl.	C_2H_5Cl.	H_2O.	α.
100	33·00	—	69·26	2·26	30·74	30·74	0·166
100	33·00	107·66	75·82	8·82	24·18	131·84	0·210*
100	33·00	27·10	71·28	4·28	28·72	55·82	0·190
100	31·16	—	70·95	2·11	29·05	29·05	0·177
100	31·16	22·08	72·23	3·39	27·77	49·85	0·177
100	31·16	31·97	72·60	3·76	27·40	59·37	0·168
100	31·83	—	70·41	2·24	29·59	29·59	0·180
100	31·83	47·89	72·58	4·41	27·42	75·31	0·155*
100	31·83	23·77	71·68	3·51	28·32	52·09	0·171
100	31·83	—	70·39	2·22	29·61	29·61	0·178

Average α=**0·176**, rejecting the results when two layers were formed.

100	23·17	—	78·21	1·38	21·79	21·79	0·227
100	25·74	—	75·99	1·73	24·01	24·01	0·228
100	25·74	19·77	77·09	2·83	22·91	42·68	0·223
100	25·74	38·77	77·90	3·64	22·10	60·87	0·211
100	25·18	—	76·56	1·74	23·44	23·44	0·243
100	24·66	—	77·08	1·74	22·92	22·92	0·255
100	24·66	19·53	78·02	2·68	21·98	41·51	0·229
100	24·66	25·65	78·27	2·93	21·73	47·38	0·223

Average α=**0·230**.

* Two layers formed.

Equilibrium at 77°.

In this case the tubes were heated for five weeks in order to be sure that equilibrium was reached; to make additionally certain, some of the tubes were first heated for a few days at 99° and after that at 77°. The following will indicate the agreement obtained:

Wt. of mixture.	Time of heating.	Titre in c.c. baryta.	Titre for 1 gram.
2·1442 grams	April 13—May 15	8·62	4·02
2·2207 ,,	April 13—15 at 99°	9·01	4·06
2·3375 ,,	and then until May 15 at 77°	9·40	4·02

C_2H_5·OH.	HCl.	C_2H_5·OH.	HCl.	C_2H_5Cl.	H_2O.	α.
100	23·17	79·34	2·51	20·66	20·66	0·467
100	25·74	76·98	2·72	23·02	23·02	0·395
100	31·16	72·14	3·30	27·86	27·86	0·307

Later on some fresh determinations were made, the temperature in this case being 76·3—76·5°.

Equilibrium at 76·5°.

$C_2H_5{\cdot}OH$.	HCl.	$C_2H_5{\cdot}OH$.	HCl.	C_2H_5Cl.	H_2O.	a.
100	9·76	91·29	1·05	8·71	8·71	1·263
100	14·26	87·36	1·62	12·64	12·64	0·886
100	16·78	85·12	1·90	14·88	14·88	0·730
100	21·20	81·43	2·63	18·57	18·57	0·620
100	23·45	79·24	2·69	20·76	20·76	0·495
100	27·35	75·91	3·26	24·09	24·09	0·426
100	28·86	74·52	3·38	28·86	28·86	0·302
100	40·84	63·43	4·27	36·57	36·57	0·226

In each case a has been calculated according to the formula

$$a = \frac{\text{alcohol} \times \text{acid}}{\text{ester} \times \text{water}},$$

where alcohol = concentration of alcohol expressed in equivalents, and similarly for acid, ester, and water.

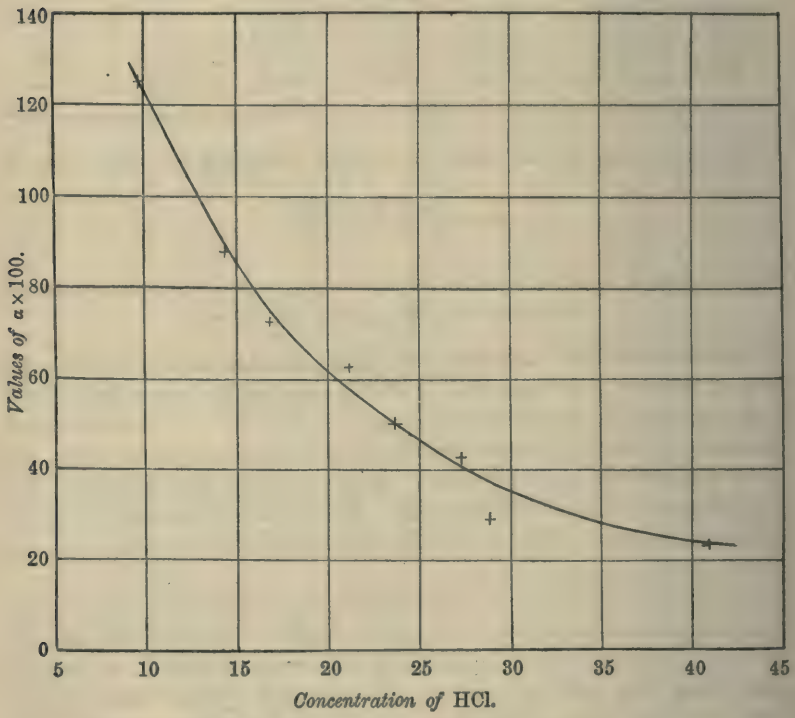
The results at 99° have been arbitrarily divided into two series, for one of which the average of a is 0·176, and for the other 0·230; the concentration of the hydrochloric acid in the reaction mixture used (column 2) remains practically the same throughout each series, but it is different in the two series. Accompanying this difference is a variation of a from 0·176 to 0·230. The variations in each series are irregular, and are probably for the most part within the limit of the error of experiment.

The parallelism between the concentration of the hydrochloric acid (column 2) and the value of a no longer holds if we take the concentrations of the acid when equilibrium was reached, as will be seen by comparing the numbers in the fifth column of the table for 99°. Similar results were obtained at 129·5°, but the figures are not given as they are not so trustworthy, owing to the formation of two layers. This variation of a with the amount of hydrochloric acid present is shown much better by the determinations at 77° and 76·5°, as at these temperatures the value of a is much more sensitive to alterations in the concentration of the hydrochloric acid than is the case at higher temperatures. The curves given in Figs. 2 and 3 illustrate these results, and do not need further explanation. From them we can deduce that "the value of a *decreases* with *increasing* concentration of the hydrochloric acid." This is true whether we take the concentrations of the acid at the

beginning of the experiment (Fig. 2), or when equilibrium is reached (Fig. 3).

There are several causes which may bring about this result. The concentrations of the alcohol, acid, &c., have been taken as representing their active quantities, and the equation for the equilibrium constant was developed on this assumption. This is, however, only strictly true in dilute solutions. Arrhenius (*Zeit. physikal. Chem.*, 1899, **28**, 317) has shown that better results are obtained when the osmotic pressure is used instead of the concentration; owing to the lack of

FIG. 2.



the necessary data, it is impossible to put this to the test. It is doubtful if this would account for the variations in α, as van't Hoff has shown that in the analogous case of alcohol and acetic acid fairly good constants are obtained.

Alcohol has a tendency to form double molecules; the same is true of water, but to a much greater extent, and this may affect the value of α. In each series at 99°, however, the presence of water does not seem to affect the value of α, as it should do when so many double molecules are calculated as single ones.

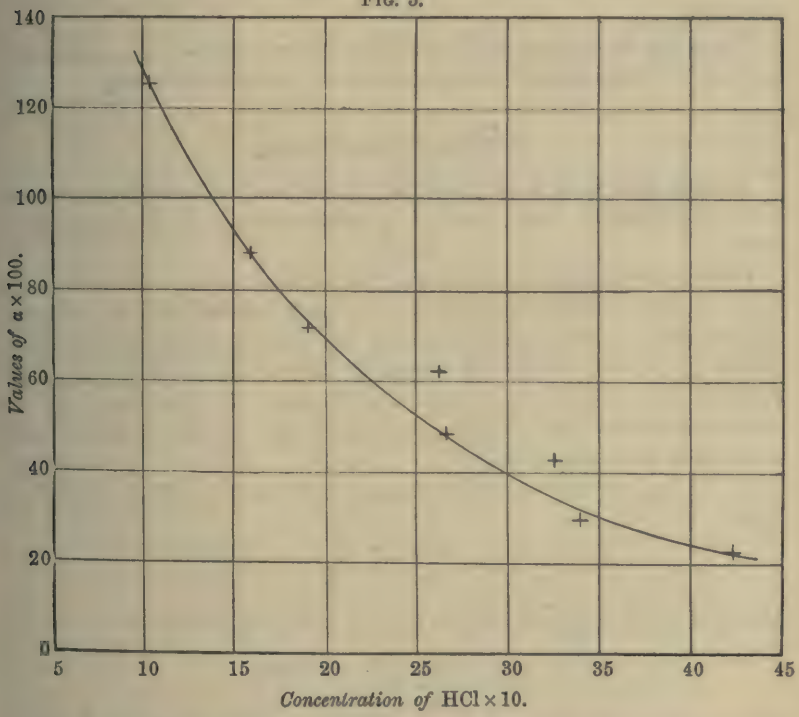
The variation of the medium and the catalytic effect of the hydrogen ions will be discussed later on.

The decrease of α as the temperature rises confirms the results of Villiers and Cain :

Ratio of alcohol to acid.	100 : 31·16.	100 : 23·17.	100 : 25·74.
Value of α at 77°	0·307	0·467	0·395
,, ,, 99°	0·177	0·227	0·228
,, ,, 129·5°	(0·087)	(0·108)	(0·100)*

* The numbers in brackets only denote the approximate value of α, as two layers were formed at the point of equilibrium.

FIG. 3.



The heat of reaction can be calculated in the usual manner from the equation

$$\frac{d}{dT}\log_e\alpha = -\frac{Q}{RT^2},$$

where Q = heat given out during the reaction when no external work is done.

Integrating this on the assumption that the heat of reaction is independent of the temperature, we have for the temperatures T_1 and T_2

$$Q = - \frac{4{\cdot}584(\log \alpha_1 - \log \alpha_2)T_1T_2}{T_1 - T_2} \text{ calories,}$$

when the calculations are made with ordinary logarithms, and R is expressed in heat units ($=1{\cdot}991$). On calculating Q from the values of α obtained at 77° and 99°, we have

From 100 C_2H_5OH : 31·16 HCl. $Q = +6489$ calories.
„ 100 C_2H_5OH : 25·74 HCl. $Q = +6475$ „
„ 100 C_2H_5OH : 23·17 HCl. $Q = +8500$ „

The first two values of Q agree very well, although the constants are taken from two different series, but the third value is altogether different.

Using the data given in Berthelot's "Thermochimie," Q is calculated to be 6750 Calories, but the figures are not very satisfactory.

Velocity of Esterification.

Villiers and Cain both measured the velocity of esterification, but their experiments were more of a qualitative than a quantitative nature.

Goldschmidt (*loc. cit.*) has shown that in the reaction between benzoic acid and ethyl alcohol, hydrochloric acid acts catalytically, the velocity of esterification being proportional to the amount of hydrochloric acid present. In the case of the action of alcohol on trichloroacetic acid (alcohol in excess and no other acid present), he shows that the trichloroacetic acid acts autocatalytically. The reverse reaction was considered to be negligible.

In the case of the action of hydrochloric acid on ethyl alcohol we have

$$\underset{A}{C_2H_5{\cdot}OH} + \underset{B}{HCl} \rightleftarrows \underset{C}{H_2O} + \underset{D}{C_2H_5Cl}$$

and this gives us $\frac{dx}{d\theta} = k_1(A-x)(B-x) - k_2(C+x)(D+x)$

$$\text{and } \alpha = \frac{k_2}{k_1} = \frac{(A-x)(B-x)}{(C+x)(D+x)}$$

as used in the first part of the paper.

On calculating the constants from Cain's numbers (*loc. cit.*) according to the above equation, the results showed plainly that it did not represent the true course of the reaction as the "constants" decreased very

rapidly. The probable reason of this is that the acid acts autocatalytically, and this action must be taken into account.

Ostwald (*Lehrbuch der allgem. Chemie*, 2 Aufl., 2^2, 263) represents the acceleration due to a catalyser by an additive term in the velocity equation. In the case of a single substance which acts on itself catalytically, he writes the equation as

$$\frac{dx}{d\theta} = \{k_1 + k_2(A-x)\}(A-x),$$

where k_1 = velocity coefficient if no catalyser is present,
k_2 = „ „ due to catalyser.

Now, in most cases of autocatalysis, the constant k_1 becomes indefinitely small in comparison with k_2, and can be neglected. The above equation then becomes

$$\frac{dx}{d\theta} = k_2(A-x)^2.$$

In the reaction between hydrochloric acid and ethyl alcohol, the hydrogen ions only act autocatalytically in the direct reaction; the reverse reaction would take place very slowly, however, if it were not catalytically influenced by the acid present (compare the rate of catalysis of methyl acetate by water alone and in the presence of hydrochloric acid), and in this case also we can neglect the amount of ester which would be formed if no catalyser were present. We may therefore write the velocity equation as

$$\frac{dx}{d\theta} = k'p(A-x)(B-x)^2 - k''p(B-x)(C+x)(D+x),$$

since the concentration of the hydrogen ions is given by that of the dissociated part of the acid, that is, by $p(B-x)$ where p is a function of the concentration $(B-x)$. This function would generally be represented by Ostwald's dilution law $\frac{p^2}{1-p} = \beta v = \frac{\beta}{B-x}$ where β is the conductivity constant, or by some such formula as that of Rudolphi (*Zeit. physikal. Chem.*, 1895, **17**, 385) or Bancroft (*ibid.*, 1899, **31**, 188), but in the present case it is almost impossible to find an equation for it, as the composition of the medium is continually changing. We can, however, assume that the concentration of the hydrogen ions is proportional to the amount of acid present, that is, the dissociation of the hydrochloric acid is considered to be constant during the time of experiment. The reaction equation then becomes

$$\frac{dx}{d\theta} = k_1(A-x)(B-x)^2 - k_2(C+x)(D+x)(B-x).$$

If no ester is present to begin with, $D=0$ and

$$\frac{dx}{d\theta}=k_1\{(A-x)(B-x)^2-ax(C+x)(B-x)\} \text{ where } k_2=ak_1.$$

Integrating this on the assumption that when $x=0$, $\theta=0$, we have

$$\frac{A+aC-B(1-2a)}{\sqrt{P}}\log_e\frac{x\{A+B+aC-\sqrt{P}\}-2AB}{x\{A+B+aC+\sqrt{P}\}-2AB}$$

$$-\log_e\frac{1}{AB}\{x^2(1-a)-x(A+B+aC)+AB\}+2\log_e\frac{B-x}{B}$$

$$=2aB(B+C)k_1\theta.....(3)$$

where $P=(A+B+aC)^2-4AB(1-a)$.

Goldschmidt (*loc. cit.*) found that satisfactory constants were obtained if the reverse reaction were neglected. In the present case, the value of k_2 is only about one-fifth of k_1 ($a=0{\cdot}176$ or $0{\cdot}230$), so that the reverse reaction will have a much less velocity than the direct one, and when it is in its first stages and x and $(C+x)$ are very small, it is probable that the term due to the reverse reaction can be neglected. We then have for the velocity equation

$$\frac{dx}{d\theta}=k(A-x)(B-x)^2,$$

or on integration,

$$\frac{(A-B)x}{B(B-x)}+\log_e\frac{A(B-x)}{B(A-x)}=(A-B)^2k\theta.....(4)$$

Donnan (*Ber.*, 1896, **29**, 2422) has shown that the same form of reaction equation as Goldschmidt used for the reaction between trichloroacetic acid and alcohol is obtained on the assumption that the reaction takes place between the alcohol and the ions of the acid; that is to say, there is no need to assume that the acid acts autocatalytically. However, the experiments of Knoblauch on the reaction between ethyl alcohol and acetic acid in the presence of hydrochloric acid, and of Goldschmidt on the reactions between (1) ethyl alcohol and benzoic acid in the presence of hydrochloric acid, (2) ethyl alcohol and phenylacetic acid in the presence of picric acid and the *p*-toluidine salt of picric acid, seem to show that the foreign acid acts catalytically. Goldschmidt has also shown that the equilibrium between ethyl alcohol and acetic acid is affected by picric acid (which is a foreign acid and acts catalytically) in the same way as the equilibrium between hydrochloric acid and ethyl alcohol is affected by the acid.* We may

* Where picric acid is the catalyser, this variation of the equilibrium may be due to the alteration in the medium (compare Koelichen, *Zeit. physikal. Chem.*, 1900, **33**, 129) but with hydrochloric acid, this explanation would not seem to hold, both

therefore assume for the present that the hydrochloric acid in the latter reaction acts autocatalytically.

From the first form of the velocity equation we again get

$$a = (A - x)(B - x)/(C + x)(D + x).$$

Zaitschek (*Zeit. physikal. Chem.*, 1897, **24**, 1), in the course of his investigations on the equilibrium between sulphuric acid and alcohol, has also found that the equilibrium constant a (calculated as above) depends on the amount of acid present. He explains it on the assumption that the hydrogen ions act catalytically, but that their influence is greater in the direct than in the reverse reaction. The decrease of a with the increase of the amount of acid then follows as a matter of necessity, because the value of a is simply the ratio of the velocity constants of the reverse and direct reactions ($k_2 = ak_1$).

According to the second law of thermodynamics, we can prove that "if a reaction which proceeds to a state of equilibrium is catalytically influenced, the reverse reaction must also be influenced to the same extent, and therefore the value of a will not alter" * (Ostwald, *Grundriss*, 2te Aufl., p. 519). This only holds for the extreme case when we can (theoretically) introduce the catalyser at the beginning of the reaction and take it out again at the end, so that the sum of the work done is zero. In the present case ($C_2H_5 \cdot OH$ and HCl), it is doubtful if this condition is fulfilled, because the catalyser is an auto-one, and one of the components of a system which is in equilibrium cannot be added or taken away without disturbing it.

Zaitschek's explanation is really as follows: the velocity equation can be written as

$$\frac{dx}{d\theta} = k'(A - x)(B - x)k_3(B - x) - k''(C + x)(D + x)k_4(B - x),$$

k_3 and k_4 representing the catalytic coefficients in the direct and reverse reactions respectively. For equilibrium, we then have

$$\frac{dx}{d\theta} = 0 \text{ and } \frac{(A - x)(B - x)}{(C + x)(D + x)} = \frac{k''k_4}{k'k_3} = a = \frac{k_2}{k_1};$$

k' and k'' are constants; a, we know, diminishes as the amount of hydrochloric acid increases, that is, the ratio of $k_4 : k_3$ does not remain constant, but decreases as $(B - x)$ increases; in other words, the law

Goldschmidt and Knoblauch finding that the equilibrium in aqueous solution alters with the concentration of the acid (catalyser) present, although the variation in the amount of the same would not affect the medium very much. Similarly, in the reaction between ethyl alcohol and hydrochloric acid, we may assume that the variation in a is not *primarily* caused by the variation in the medium.

* Koelichen has shown this to be the case in the condensation of acetone to diacetonealcohol by means of sodium hydroxide (*Zeit. physikal. Chem.*, 1900, **33**, 129).

which connects the concentration and catalytic effect of the hydrogen ions is different in the direct and reverse reactions. This may very well be the case, as in the direct reaction the acid acts auto-catalytically, and in the reverse reaction as an ordinary catalyser.

Measurements of Velocity.

Owing to the conditions of experiment, the reaction mixture cannot be warmed up to the required temperature before the reaction is allowed to begin. The measurement of the time (θ) is thus subject to an error due to the warming and cooling of the tubes at the beginning and end of the experiment. This error can be obviated by reckoning θ from the time when the first tube is taken out of the thermostat.*

Then, if the value of $k\theta_0$ for the first tube is V_0, and the value of $k\theta_1$ for the second tube is V_1, the true value of k is given by $\frac{V_1 - V_0}{\theta_1 - \theta_0}$.

In the following tables,

A = amount of alcohol used, expressed in equivalents.
B = „ hydrochloric acid used, expressed in equivalents.
C = „ water „ „ „
x = „ ester formed „ „ „
θ = time in minutes, reckoned from when tubes were immersed.
a = equilibrium constant.
κ_1 = $2aB(B+C)k_1$ = constant calculated according to equation (3), page 314.
κ = $(A-B)^2k$ = constant calculated according to equation (4), page 314.

} taking first measurement as starting point.

All the calculations have been made with Briggs' logarithms, and are expressed accordingly.

* To obtain the greatest degree of accuracy, each value of θ should separately be taken as the starting point for succeeding measurements; this does not affect the results, however, except in the cases where C has a value different from zero. It will be seen that in these cases the values of the constants vary, and can only be used for qualitative comparison, so that the extra calculation is unnecessary.

Results at 99°.

$A=100.$ $B=33{\cdot}00.$ $C=0.$ $a=0{\cdot}176.$

θ.	x.	$\kappa_1\times10^6$.	$\kappa\times10^4$.	$k_3\times10^{7}$*.
35	10·34	—	—	—
60	14·51	771	204	410
85	17·25	761	203	376
110	19·25	777	203	352
138	20·77	763	197	322
174	22·56	787	203	309
214	23·62	772	193	278

$\therefore\ \kappa_1\times10^6 = 774$†. $\quad\therefore\ \kappa\times10^4 = 201$†.

$\therefore\ k_1\times10^9 = \mathbf{2019}$. $\quad\therefore\ k\times10^8 = \mathbf{448}$.

$A=100.$ $B=41{\cdot}33.$ $C=0.$ $a=0{\cdot}103$‡.

θ.	x.	$\kappa_1\times10^6$.	$\kappa\times10^4$.
16	8·26	—	—
33	14·29	689	154
49	18·12	697	156
62	20·45	703	154
77	22·47	698	154
96	24·41	691	152
120	26·53	708	154

$\therefore\ \kappa_1\times10^6 = 698.$ $\quad\therefore\ \kappa\times10^4 = 154.$

$\therefore\ k_1\times10^9 = \mathbf{1984}.$ $\quad\therefore\ k\times10^8 = \mathbf{447}.$

* For the sake of comparison, the constants have also been calculated (in thi case only) according to the formula

$$\frac{dx}{d\theta} = k_3\{(A-x)(B-x)-a(C+x)(D+x)\}.$$

It will be seen that the so-called constants are not by any means constant, but diminish rapidly, thus showing that the action of the hydrochloric acid as a catalytic agent cannot be neglected.

† Mean of the values under κ_1 and κ respectively.

‡ The value of a has been calculated from the known results on the assumption that it is proportional to the amount of hydrochloric acid present.

$A=100.$ $B=31{\cdot}83.$ $C=0.$ $a=0{\cdot}176.$

$\theta.$	$x.$	$\kappa_1\times10^6.$	$\kappa\times10^4.$
15	5·56	—	—
30	9·85	785	248
45	12·67	787	242
60	15·03	823	249
75	16·60	812	243
90	18·08	834	247
105	19·08	822	243
128	20·35	814	237

$\therefore\ \kappa_1\times10^6=$ 811 and $\kappa\times10^4=244$
$\therefore\ k_1\times10^9=$ **2274** and $k\times10^8=$ **525**

$A=100.$ $B=24{\cdot}66.$ $C=0.$ $a=0{\cdot}230.$

$\theta.$	$x.$	$\kappa_1\times10^6.$	$\kappa\times10^4.$
15	3·85	—	—
30	7·08	774	353
45	9·46	777	361
60	11·21	782	361
75	12·42	760	349
90	13·55	769	352
107	14·62	783	355
121	15·16	760	344

$\therefore\ \kappa_1\times10^6=$ 772 and $\kappa\times10^4=354$
$\therefore\ k_1\times10^9=$ **2760** and $k\times10^8=$ **624**

$A=100.$ $B=23{\cdot}17.$ $C=0.$ $a=0{\cdot}230.$

18	4·58	—	—
30	6·68	651	357
61	10·41	673	366
62	10·57	685	373
77	11·77	686	372
90	12·58	681	368
92	12·76	690	372
107	13·51	683	367

$\therefore\ \kappa_1\times10^6=$ 678 and $\kappa\times10^4=369$
$\therefore\ k\times10^9=$ **2746** and $k\times10^8=$ **625**

$A=100.$ $B=33{\cdot}00.$ $C=107{\cdot}66.$ $a=0{\cdot}176.$

35	3·55	—	—
78	6·61	713	43·3
147	10·02	695	41·2
193	11·54	668	39·0
246	13·11	665	38·1
369	15·35	(616)	(34·1)
474	16·90	(609)	(32·6)

$\therefore\ \kappa_1\times10^6+685$ and $\kappa\times10^4=40{\cdot}4$*
$\therefore\ k\times10^9=$ **419** and $k\times10^8=$ **90**

* Results below the dotted line are not included in the average.

$A=100.$ $B=33{\cdot}00.$ $C=27{\cdot}10.$ $a=0{\cdot}176.$

30	7·84	—	—
69	13·06	940	134
102	15·73	918	129
130	17·14	867	121
169	18·90	861	118
207	20·04	832	112
246	20·89	797	106

$\therefore\ \kappa_1\times10^6=$ 869 and $\kappa\times10^4=120$
$\therefore\ k_1\times10^9=$ **1245** and $k\times10^8=$ **267**

$A=100.$ $B=24{\cdot}66.$ $C=25{\cdot}65.$ $a=0{\cdot}230.$

15	2·41	—	—
30	4·80	940	212
46	6·71	920	207
60	8·02	904	202
76	9·39	922	204
90	10·17	885	195
105	10·97	871	191
120	11·68	862	188

$\therefore\ \kappa_1\times10^6=$ 901 and $\kappa\times10^4=199$
$\therefore\ k_1\times10^9=$ **1579** and $k\times10^8=$ **351**

These results are summarised in the following table:

A.	*B.*	*C.*	$k_1 \times 10^3$.	$k \times 10^3$.
100	33·00	—	202	448
100	41·33	—	198	447
100	31·83	—	227	525
100	33·00	107·66	42	90
100	33·00	27·10	125	267
100	23·17	—	275	625
100	24·66	—	276	624
100	24·66	25·65	158	351

In those experiments where no water was present to start with, the constants are very satisfactory, indeed, better than would be expected when the change which takes place in the medium during the progress of the reaction is taken into account. The constants calculated with the formula (4) are quite as good as those calculated according to the equation (3).

The case is different, however, when water takes part in the reaction from the beginning (compare Goldschmidt, *loc. cit.*). The constants then diminish as the time increases, and although there is not much difference as regards the application of the two formulæ, the first one gives a slightly better result.

On comparison of the constants of one series with those of another (compare summarised table), the action of water in retarding the reaction is very apparent; the greater the amount of water present, the greater the retardation, although the results are not proportional. This retardation is most probably due to the alteration in the medium, as this has a great effect on reaction velocity, as shown by Menschutkin (*Zeit. physikal. Chem.*, 1890, 5, 589), Hemptinne (*ibid.*, 1899, 28, 225), and others.

The velocity constants fall into two divisions, corresponding to the two values of the equilibrium constant, excluding the cases where aqueous alcoholic solutions were used. They also diminish as the proportion of acid to alcohol increases; this may be due to an alteration in the medium, but can also be deduced as follows:

The constant k_1 is really the product of two factors, namely, k, the true velocity constant, and a factor depending on the dissociation of the acid. In writing down the velocity equation, the concentration of the hydrogen ions has been taken as being simply proportional to the amount of acid present, that is, proportional to $(B-x)$, so that we may write the concentration as $c(B-x)$, where c* is a constant. The

* This c is a true constant and not a function of the concentration as in Ostwald's dilution law. It varies with each experiment, but during each one is taken as constant, this being the assumption on which the velocity equation was formulated.

velocity equation is then

$$\frac{dx}{d\theta} = kc(A-x)(B-x)^2 - k'cx(C+x)(B-x)$$
$$= k_1(A-x)(B-x)^2 - k_2x(C+x)(B-x),$$

where $k_1 = kc$, and $k_2 = k'c$.

Now, for two different solutions, k and k' will remain the same, but c will vary. If the values of k_1 for these two solutions are $(k_1)_a$ and $(k_1)_b$, and of c are $(c)_a$ and $(c)_b$, we have $(k_1)_a = k(c)_a$, and $(k_1)_b = k(c)_b$; therefore, if $(c)_a > (c)_b$, then $(k_1)_a > (k_1)_b$. Similarly for k_2. Now the more dilute the solution of hydrochloric acid in alcohol is, the more the dissociation increases, that is, the value of c increases as the proportion of acid diminishes, and therefore the value of k_1 must act similarly, as shown by the table. Thus, only constants can be compared with each other in those experiments in which the proportion of acid present is the same or approximately the same. Since the two formulæ give equally good constants, it follows that the reverse reaction takes place so slowly (at least during the time of experiment) that it may be neglected.

Velocity at 77°.

The equilibrium constants in the particular mixtures used were not determined directly, owing either to the breaking of the tubes before equilibrium was reached, or to the formation of two layers. They have been calculated from the constants of the mixtures with 31·16 and 25·74 equivalents of HCl respectively, and cannot be far from correct, as may be seen by comparison with the values obtained at 76·5°.

$A=100.$ $B=33·00.$ $a=0·28.$				$A=100.$ $B=41·33.$ $a=0·18.$			
θ.	x.	$\kappa_1 \times 10^6$.	$\kappa \times 10^5$.	θ.	x.	$\kappa_1 \times 10^6$.	$\kappa \times 10^5$.
60	3·20	—	—	20	6·76	—	—
146	7·12	172	280	50	8·73	169	217
248	10·09	153	259	90	10·93	174	214
412	13·61	151	253	137	13·19	169	216
				196	15·68	174	223
				238	17·03	173	220
				282	18·32	173	220
$\therefore$ $\kappa_1 \times 10^6 = 159$ and $\kappa \times 10^5 = 264$.				$\therefore$ $\kappa_1 \times 10^6 = 172$ and $\kappa \times 10^5 = 218$.			
$\therefore$ $k_1 \times 10^9 = 261$ and $k \times 10^8 = 59$.				$\therefore$ $k_1 \times 10^9 = 280$ and $k \times 10^8 = 63$.			

The following table gives a comparison of the results at 99° and 77°:

Temperature.	A.	B.	$k_1 \times 10^8$.	$k \times 10^8$.
99°	100	33	202	448
77	100	33	26	59
99	100	41·33	198	447
77	100	41·33	28	63

The influence of temperature on the reaction velocity is thus very great, a rise in the former of 22° increasing the latter to between seven and eight times its former value. According to Arrhenius (*Zeit. physikal. Chem.*, 1889, 4, 226), the influence of temperature on the velocity of reaction may be represented by the equation

$$\frac{d}{dT} log_e k = \frac{A}{T^2},$$

or, integrated on the assumption that A is independent of the temperature $log_e k = -\frac{A}{T} + B$, where A and B are constants.

On calculating the value of A from the results given above we find :

Mixture.	From k_1.	From k.
100 : 33	12134	11998
100 : 41·33	11576	11596

The values agree as closely as could be expected. In the case of the simple esters of organic acids, A has been found to be about 8670 (compare Price, *Öfvers. Kongl. Vet.-Ak. Förhand.*, 1899, No. 9, 932), so that the influence of temperature is much greater in the present case.

So far it has not been found practicable to measure the velocity of the reverse reaction. That the same equilibrium constant is obtained has already been shown by Villiers and Cain.

It gives me great pleasure to express here my indebtedness to Prof. Arrhenius at Stockholm, and Prof. Frankland, at Birmingham, for the facilities afforded me during my work.

XXXIII.—*The Collection and Examination of the Gases produced by Bacteria from certain Media.*

By Walter Charles Cross Pakes and Walter Henry Jollyman.

During the course of an investigation upon the bacterial flora of the water of a certain well, several specimens of bacteria were isolated which belonged to the group of *Bacillus fluorescens liquefaciens*. The determination of the cultural reactions enabled us to divide these into two groups, (1) that which produced gas, and (2) that which produced no gas in media containing nitrate. These were provisionally designated S.O.7 and S.O.6 respectively. In order to obtain more information concerning the former of these, it was decided to analyse the gas produced.

As the various forms of apparatus hitherto described for the purpose of the collection of gas thus produced did not seem to be sufficiently accurate or suitable for our purpose, we designed one which is both simple and accurate.

It was necessary to have an apparatus which fulfilled the following conditions:

(1) A relatively large amount of medium must be used—from 300 to 500 c.c.

(2) The gas receiver must have a capacity of at least 600 c.c.

(3) It must be easy to inoculate the medium without any chance of accidental contamination.

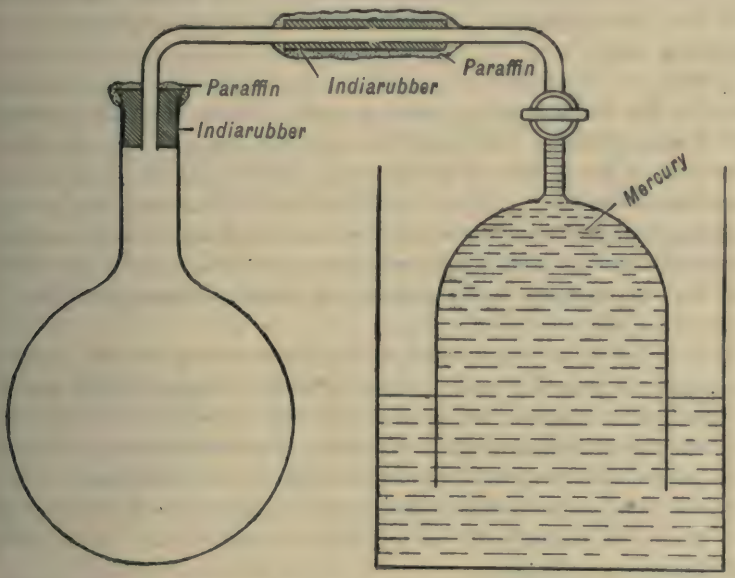
(4) The receiver must be fitted with taps so that a part or the whole of the gas can be removed during the course of the experiment without chance of contamination.

(5) Every part must be capable of effective sterilisation both before inoculation and at the conclusion of the experiment.

In our apparatus, the receiver is a bell-jar made of stout glass about 14 cm. high and 9 cm. in diameter. At the apex a glass tube is fused in; this rises vertically 5 cm., and is then bent at right angles, the arm being about 10 cm. long. Halfway along the vertical tube is a three-way tap placed horizontally. This receiver is placed in an iron cylinder three parts full of mercury, about 35 pounds of mercury being required for each apparatus. The flask containing the medium is an ordinary one of from 300 to 1500 c.c. capacity, and in this are placed from 100 to 400 c.c. of the medium. The mouth is fitted with a rubber stopper perforated in the centre, and carrying a tube bent at right angles; this carries a piece of pressure tubing about three inches long, which is plugged with a small piece of cotton-wool at the open end.

When the apparatus is to be used, the mercury in the receiver is

sucked up into the tap, which is then shut off. The open end of the three-way tap is plugged with melted paraffin wax, and the empty portion of the glass tube filled with sterile water. The inoculation is made in the usual way with a platinum needle, care being taken that the neck of the flask and the rubber stopper are thoroughly heated in a flame before and after the operation. The cotton-wool plug is removed from the end of the rubber tubing, and the free end of the latter is slipped on to the arm of the receiver. All the connections, including the three-way tap after it has been turned so as to connect the flask with the receiver, are carefully painted with melted paraffin wax. When the tap is turned, the mercury naturally falls in the receiver, and the



height of the mercury may be marked when the temperature of the whole apparatus is that of the incubator.

In order to test the apparatus, we performed several blank experiments. We filled the flask with water, connected it with the receiver, and then withdrew a certain quantity of mercury from the reservoir so that the difference between the levels of the mercury was between four and five inches. We then allowed the apparatus to stand in the laboratory for a week, and examined it daily. At the end of the time there was absolutely no fall in the mercury. On nine occasions, we have inoculated media for the purpose of determining whether any gas was produced, and although the growth has been allowed to continue for upwards of a week—in one case three weeks—there was no trace of

gas in the receiver. These trial experiments, taken in conjunction with the fact (p. 329) that no oxygen was found in the receiver in the experiments with the *B. coli communis* in sugar-containing media, show that the apparatus is air-tight, and that there is no chance of air getting into the receiver during an experiment. It is possible that a certain amount of carbon dioxide may be absorbed by the indiarubber, but as the two glass tubes which are joined by the rubber tubing are in actual contact, the amount absorbed by this must be infinitesimal. A certain small amount may be absorbed by the indiarubber stopper, but we do not see how this can be avoided.

In order to examine the gas produced, as it may be inaccurate to take a sample from the receiver, it is necessary to mix the gas in the flask with that in the receiver. This may be rapidly accomplished in the following way.

Connect an Orsat, or some similar gas apparatus (working with mercury) to the three-way tap, remove about 100 c.c. from the receiver, and then, reversing the three-way tap, force the gas into the flask. Now remove about 100 c.c. of the mixed gases from the flask and replace in the receiver. Repeat this three or four times and the gas will be homogeneous throughout. If it is required to have an atmosphere containing an excess of oxygen, a measured volume may be introduced into the receiver from a gas analysis apparatus, and may be mixed in the manner above detailed.

If it is desired to experiment with an atmosphere of pure oxygen, the stopper is provided with a second glass tube through which oxygen is passed after the fluid has been inoculated, care being taken that it is previously filtered through cotton-wool. The tube is finally sealed off.

In order to be prepared to examine small quantities of gas, we used a special Orsat apparatus provided with two gas tubes of extra length and graduated throughout, containing 120 and 60 c.c. respectively, both being water-jacketed.

Experiment No. 1.—Two hundred c.c. of meat extract (that is, the extract of 1 lb. of lean meat in 1 litre of water), containing 1 per cent. of ammonium nitrate and 0·5 per cent. of common salt, were placed in a flask of 350 c.c. capacity. After having been sterilised, it was inoculated with a trace of an agar culture of the S.O.7.

The apparatus was placed in the incubator at 20°, and after 2 hours the level of the mercury was marked. On the following day there was no sign of gas in the flask, although there was an abundant growth, but the level of the mercury in the gas jar had risen about half an inch. This decrease in the volume of the gas is due to the fact that the oxygen is taken up by the bacteria in the first stage of the experiment.

On the succeeding day, there was an abundant evolution of gas, and

the level of the mercury was lower than at the commencement of the experiment.

At the end of four days, the evolution of gas had ceased, and there were 150 c.c. in the receiver. This was analysed, and gave the following result:

Carbon dioxide	9·3 per cent.
Oxygen	0·6 „
Nitrogen	90·1 „

Since the original 150 c.c. of air contained approximately 120 c.c. of nitrogen and 30 c.c. of oxygen, there was

A loss of oxygen	amounting to	28 c.c.
A gain of nitrogen	„	150 „
A „ of carbon dioxide	„	28 „

A second experiment with the same medium and under the same conditions gave

A loss of oxygen	amounting to	33 c.c.
A gain of nitrogen	„	112 „
A „ of carbon dioxide	„	21 „

The facts that although a considerable amount of the oxygen appeared to have been used up before there was any production of gas, and that the organism was still able to grow, suggested that bacteria might be able to obtain oxygen from nitrates. This suggestion was borne out when we found that exactly the same thing happened with the *B. pyocyaneus* grown upon this medium.

In order to test this theory, the *B. pyocyaneus* was grown in nitrate broth under strictly anaerobic conditions, both in Buchner's tubes and in an atmosphere of hydrogen. In every case, we found that the organism grew, so far as we could see, as well as under aerobic conditions.

As the *B. pyocyaneus* is generally considered a strictly aerobic organism (Lehmann and Neumann say that this bacillus will not grow anaerobically, and Flugge says, "Der Pyocyaneus ist ein fast obligater Aerobier"), it is obvious either that it is not a strict aerobe, or that the term anaerobe requires modification.

Our first experiments were conducted with ammonium nitrate, and thinking that the effect was possibly due to the ammonium, we next substituted potassium, sodium, lithium, and calcium nitrates, with identical results.

If the presence of nitrate in a medium renders the medium aerobic, a strict anaerobe ought not to grow in it. Broth and glucose-formate broth therefore were made, and to some of each 1 per cent. of nitrate was added. The bacilli of malignant œdema and of symptomatic

anthrax were inoculated into these, and incubated anaerobically for several days at 37°. In each of the broth and glucose-formate broth tubes, abundant growth had taken place, but in none of the tubes containing nitrate was there a semblance of growth.

It may be suggested that the nitrate really acts as a poison to these bacteria, but if this is so, it seems strange that so many bacteria, including many which grow either aerobically or anaerobically, grow as well in broth containing nitrate as in simple broth, and that some, such as *B. anthracis* and *Streptococcus* often grow better.

The term anaerobe must therefore be extended, and it must be understood that an anaerobic organism is one which will not grow in the presence either of free oxygen or of available oxygen in the form of nitrates. The meaning of the term aerobe must be similarly extended.

The gas produced by the *B. pyocyaneus* when grown under anaerobic conditions was next examined. Instead of using some inert gas, such as nitrogen in lieu of air, we determined to eliminate all gas from the apparatus. In order to accomplish this, the following method was adopted.

The medium, about 450 c.c., is placed while very hot in a strong round-bottomed Jena flask, which is filled to the top and is fitted with a good indiarubber stopper, through which passes a piece of manometer tubing bent at right angles; each arm is about 5 cm. in length. The free end of this is connected by means of pressure tubing with a second piece of tubing also bent at right angles, the short arm being about 5 cm., and a longer arm about 20 cm. in length. The longer arm passes through a plug of cotton wool into an Erlenmeyer flask of about 150 c.c. capacity containing 100 c.c. of the medium. The two flasks thus connected together are sterilised in the usual way. When the sterilising is completed, the flasks are removed at once from the steriliser and the tubing connecting them is securely clamped. As the fluid cools, it contracts, leaving an empty space in the neck of the flask. When the fluid has cooled sufficiently to be inoculated, a test-tube containing a young and vigorously growing culture of the *Bacillus* in the same nitrate medium is taken, the arm of the bent tube which is in the Erlenmeyer flask is withdrawn from the flask and inserted into the test-tube; the clamp on the rubber tubing is slightly released and a little of the culture is allowed to enter the flask. When five or six c.c. have thus been admitted, the rubber tube is again clamped and the glass tube inserted into a flask containing some recently boiled, quickly-cooled distilled water; the clamp is again released and the inoculated flask is filled entirely; the clamp is secured, and the long-armed glass tubing removed. The horizontal arm of the receiver and the free end of the rubber tubing are both filled with hot water, and

the rubber tubing is pushed on to the arm of the receiver (see fig., p. 323). In order to prevent the mercury being sucked back into the flask, care should be taken that it is warmed, and that the medium is thoroughly cooled.

Experiment No. 3.—A flask containing 425 c.c. of meat extract, with 1 per cent. of ammonium nitrate and 0·5 per cent. of common salt, was inoculated with the *B. pyocyaneus* and incubated at 37°.

After four days, when there was no further sign of gas production, the gas was removed 100 c.c. at a time and analysed. The total amount of the gas at the temperature of the laboratory was 469·3 c.c., which was found to contain :

59·6 c.c. of carbon dioxide.
2·5 ,, oxygen.
407·2 ,, nitrogen.

The medium was very alkaline after the experiment.

Neither the carbon dioxide nor the oxygen was anticipated, and further experiments were therefore undertaken to ensure the correctness of the result.

Grimbert (*Ann. Inst. Pasteur*, 1899, 13, 67) found that the *B. pyocyaneus* when grown in media containing nitrate gave a theoretical yield of nitrogen from the nitrate, but that no carbon dioxide was produced. He says that all this gas is combined with the base of the nitrate to form the corresponding carbonate.

This experiment differed in three respects from those of Grimbert, first he used peptone solution instead of broth containing meat extract, secondly he employed potassium nitrate and we employed ammonium nitrate, and thirdly, his experiment was begun under aerobic conditions. The experiments were therefore repeated under conditions as similar to his as possible.

Experiment No. 4.—Four hundred and twenty-five c.c. of meat juice containing 1 per cent. of Witte's peptone, 1 per cent. of ammonium nitrate, and 0·5 per cent. of common salt, inoculated with the *B. pyocyaneus* and grown anaerobically produced, after four days, 268 c.c. of gas having the following composition :

Carbon dioxide, 10·9 ; oxygen, 0·3 ; nitrogen, 88·6 per cent.

A second experiment (No. 5) with the same medium gave gas containing

Carbon dioxide, 11·1 ; nitrogen, 88·4 per cent.

Next, potassium nitrate was substituted for ammonium nitrate.

Experiment No. 6.—One hundred and fifty c.c. of meat extract containing 1 per cent. of potassium nitrate and 0·5 per cent. of common salt were placed in a flask of 360 c.c. capacity, inoculated with *B.*

pyocyaneus and grown aerobically. The analysis of the gas at the end of the experiment showed:

A loss of oxygen amounting to 40·6 c.c.
A gain of nitrogen „ 114·7 „
A „ of carbon dioxide „ 28·6 „

Experiment No. 7.—Three hundred c.c. of the same medium were placed in a flask of 750 c.c. capacity. The analysis showed:

A loss of oxygen amounting to 68·7 c.c.
A gain of nitrogen „ 264·6 „
A „ of carbon dioxide „ 46·7 „

The same medium inoculated with the *B. pyocyaneus* and grown anaerobically produced gas containing

Carbon dioxide, 23; oxygen, 1·7; nitrogen, 75 per cent.

A further experiment on exactly similar lines gave gas with the following composition:

Carbon dioxide, 12·8; oxygen, 0·7; nitrogen, 86·4 per cent.

To the medium used in the last two experiments 1 per cent. of Witte's peptone was added, and the gas produced was found to contain:

Carbon dioxide, 10·2; oxygen, 0·6; nitrogen, 89·2 per cent.

Grimbert's results were obtained with Cola's peptone. We were unfortunately unable to obtain any of this at the time, but we tried experiments with Chapoteau's peptone.

Experiment No. 11.—Four hundred and ninety c.c. of distilled water containing 1 per cent. of potassium nitrate, 1 per cent. of peptone, and 0·5 per cent. of common salt, were inoculated with the organism and in the resulting gas there was 4·5 per cent. of carbon dioxide. The growth on this occasion was not so abundant as usual, probably owing to the use of distilled water.

As Grimbert did not analyse the gas obtained in his experiments until the organism had been growing for 34 days, we analysed the gas produced at the end of each day.

Experiment No. 12.—Four hundred and sixty-five c.c. of meat extract containing 1 per cent. of peptone, 1 per cent. of potassium nitrate, and 0·5 per cent. of common salt were inoculated and incubated anaerobically on the 10th of the month.

On the 14th, 156 c.c. of gas were found of the composition:

Carbon dioxide, 13·4; oxygen, 0·4; nitrogen, 86·2 per cent.

On the 15th, 104·8 c.c. of gas containing:

Carbon dioxide, 11·0; oxygen, 0·4; nitrogen, 88·6 per cent.

On the 16th, 104 c.c. of gas containing:

Carbon dioxide, 11·6; oxygen, 0·4; nitrogen, 88·0 per cent.

On this day, all the gas was not removed, about 30 c.c. being left.

On the 20th, all evolution of gas appeared to have ceased; 59 c.c. of gas were collected and were found to contain:

Carbon dioxide, 7·6; oxygen, 0·4; nitrogen, 92·0 per cent.

Although the apparatus was left for a further two days, there was no more gas, and the medium was tested for alkalinity, which was found to be equal to 120 c.c. of decinormal soda per 100 c.c. There was no reaction for nitrites.

We cannot but conclude, therefore, that Grimbert was wrong in stating that the *B. pyocyaneus* does not produce carbon dioxide from a medium containing nitrate.

The production of free oxygen and free nitrogen at the same time suggests a reaction so peculiar that we do not propose to endeavour to explain it, but to content ourselves with calling attention to the fact. There can, we think, be no doubt as to the production of the oxygen because the above analyses were carried out during the time that analyses of the gases produced by the *B. coli communis* from grape sugar were being made, and in no single case did we find any difference in the reading after the gas had been passed over the alkaline pyrogallol.

Further experiments upon this subject are being undertaken and will be published in a subsequent paper.

XXXIV.—*Tetramethylenecarbinol.*

By W. H. Perkin, jun.

During the course of an investigation on *hydroxytetramethylene*,

$$\begin{matrix} CH_2\cdot CH_2 \\ | \quad\quad | \\ CH_2\cdot CH\cdot OH \end{matrix}$$

(Trans., 1894, 65, 960), it was thought that it would be interesting to compare the properties of this substance with those of an alcohol derived from tetramethylene but containing the hydroxyl group outside the ring, and for this reason experiments were made on the reduction of the chloride of tetramethylenecarboxylic acid, in the hope that it might prove possible to prepare tetramethylenecarbinol in quantity by this means:

$$\begin{matrix} CH_2\cdot CH_2 \\ | \quad\quad | \\ CH_2\cdot CH\cdot COCl \end{matrix} + 4H = \begin{matrix} CH_2\cdot CH_2 \\ | \quad\quad | \\ CH_2\cdot CH\cdot CH_2OH \end{matrix} + HCl.$$

The result of these experiments showed that, although the reduction does proceed in this way, the yield of tetramethylenecarbinol produced is so small that a sufficiently detailed examination of its behaviour with reagents would be very difficult. It was prepared as follows.

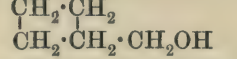
Pure ether was shaken with water until thoroughly wet and then placed on a layer of 25 per cent. caustic soda solution contained in a bottle fitted with a wide reflux condenser and standing in running water. Sodium (10 grams) cut into small pieces, was introduced all at once, and then through the top of the condenser a solution of 5 grams of tetramethylenecarboxylic chloride was run in moderately rapidly.

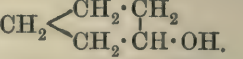
The ethereal solution from five such experiments was washed with dilute hydrochloric acid, the ether distilled off, and the residual oil, which smelt of tetramethylenealdehyde, and which had no constant boiling point, was boiled for one hour with methyl alcoholic potash in order to decompose the tetramethylenecarboxylic ester of tetramethylenecarbinol, which was evidently one of the substances formed in the reaction.

The alkaline solution was mixed with water, extracted with ether,* and the ethereal solution washed with dilute hydrochloric acid and dried over anhydrous potassium carbonate. On distilling off the ether, a small quantity of a colourless oil was obtained, which after twice fractionating distilled constantly at 143—144° under 760 mm. pressure. On analysis:

0·1912 gave 0·4872 CO_2 and 0·2026 H_2O. C = 69·5; H = 11·8.
0·1721 „ 0·4392 CO_2 „ 0·1818 H_2O. C = 69·6; H = 11·7.
$C_5H_{10}O$ requires C = 69·7; H = 11·6 per cent.

Tetramethylenecarbinol is a colourless oil which smells like amyl alcohol, and is somewhat soluble in water. It is isomeric with pentamethenyl alcohol, boiling at 139°, which Wislicenus and Hentschel (*Annalen*, 1893, 275, 322) obtained by the reduction of ketopentamethylene.


Tetramethylenecarbinol.


Pentamethenyl alcohol.

The determinations of the density, magnetic rotation and refractive power of tetramethylenecarbinol were carried out by W. H. Perkin, sen., with the following results:

Density: 4°/4° = 0·9162; 15°/15° = 0·9088; 25°/25° = 0·9029.

* By acidifying the alkaline solution and extracting with ether, almost the whole of the unreduced tetramethylenecarboxylic acid may be recovered.

Magnetic rotation.

t.	Sp. rotation.	Mol. rotation.
16·7°	1·0098	5·314.

The probable rotation of a substance of this composition may be calculated from the values of the elements thus:

C_5	= 0·515 × 5	= 2·575
H_{10}	= 0·254 × 10	= 2·540
O (as in alcohols)		= 0·194
Cal. rotation of tetramethylenecarbinol		= 5·309

The number thus obtained agrees well with that actually found.

Refractive power.

d 8·7°/8·7° = 0·9128.

	μ 8·7°.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
K	1·44096	0·48308	41·544
H_α	1·44368	0·48606	41·801
Na	1·44608	0·48869	42·027
H_β	1·45187	0·49504	42·573
H_γ	1·45645	0·50005	43·005

The calculated refractive power for H_α is obtained thus:

C_5	= 25·00
H_{10}	= 13·00
O (as in alcohols)	= 2·80
$C_5H_{10}O$	= 40·80

The value found is greater than that calculated by no less than 1·0, whereas ring compounds usually give a refractive power which is only 0·29 higher than that calculated in the above way.

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XXXV.—*The Action of Aluminium Chloride on Camphoric Anhydride.*

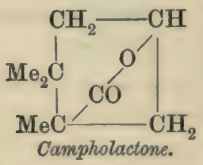
By F. H. Lees and W. H. Perkin, jun.

The behaviour of camphoric anhydride on treatment with aluminium chloride has already been made the subject of investigation, first by E. Burcker and subsequently by G. Blanc. E. Burcker (*Compt. rend.*, 1894, **119**, 426; *Bull. Soc. Chim.*, 1895, [iii], **13**, 901) studied the action of aluminium chloride on camphoric anhydride in the presence of benzene, and obtained in this way a crystalline substance, $C_{16}H_{20}O_3$, melting at 125—126°, and called by him *phenylcamphoric acid*, the corresponding yellowish liquid *anhydride*, $C_{16}H_{18}O_2$, a *ketonic acid*, $C_{15}H_{20}O_2$, which melted at 135—137°, and a *diphenyl* compound, $C_{22}H_{24}O_2$, which crystallised in reddish needles.

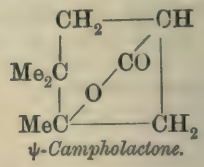
G. Blanc (*Compt. rend.*, 1896, **123**, 749; **124**, 468; *Bull. Soc. Chim.*, 1896, [iii], **15**, 1191; 1900, **23**, 693) then investigated the subject and showed that, when a solution of camphoric anhydride in chloroform is treated with aluminium chloride, an acid, $C_9H_{14}O_2$, of melting point 133°, which he subsequently identified as *isolauronolic acid*, is produced according to the equation $C_{10}H_{14}O_3 = C_9H_{14}O_2 + CO$, and this reaction now affords the most convenient method for preparing *iso*-lauronolic acid.

While we were engaged in the preparation of *iso*lauronolic acid by this process, we noticed that, besides this acid, an oil was always formed at the same time, and on investigating this, we found that it was apparently an almost pure substance, since, after twice fractionating, almost the whole quantity distilled constantly at 258° under ordinary conditions.

The analysis of this oil showed that it had the formula $C_9H_{14}O_2$, and on examination it was found to be a lactone so similar in properties to campholactone that we named it *ψ-campholactone* (Proc., 1899, **15**, 23), and suggested that the relationship between these two lactones was probably that represented by the formulæ

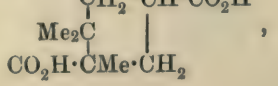


Campholactone.



ψ-Campholactone.

these formulæ being derived from



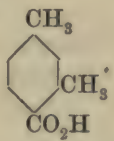
,

which at that time was considered to be the most probable expression of the constitution of camphoric acid.

As the result of a very extended investigation, we have found that this oily lactone, in spite of its remarkably constant boiling point, is a mixture of at least two isomeric lactones, $C_9H_{14}O_2$, and it appears that neither of these is directly related to campholactone. It will be seen, from the following description of our work, that we have changed our views as to the nature of this very interesting product of the action of aluminium chloride on camphoric anhydride.*

When the oily lactone is treated with baryta, it is readily hydrolysed, and the acid which is obtained by acidifying the resulting barium salt has been found to contain two hydroxy-acids of the formulæ $C_9H_{16}O_3$, which melt at 113° and 160° respectively.

Now when the original mixture of lactones or of their hydroxy-acids is dissolved in sulphuric acid and warmed at 80°, a remarkable decomposition takes place, much sulphur dioxide is evolved, and the solution on pouring into water deposits a solid acid which in each case has been proved to be *xylic acid*,



The easy transformation of these substances into xylic acid, as well as other properties which have been discovered during their investigation, leaves scarcely any doubt that they are all derivatives of hexahydro-xylic acid, and not in any direct way connected with camphoric acid; in other words, we are of opinion that the two acids, $C_9H_{16}O_3$, are stereoisomeric forms of *hydroxyhexahydro-xylic acid*,

$$OH\cdot C_6H_8(CH_3)_2\cdot CO_2H.$$

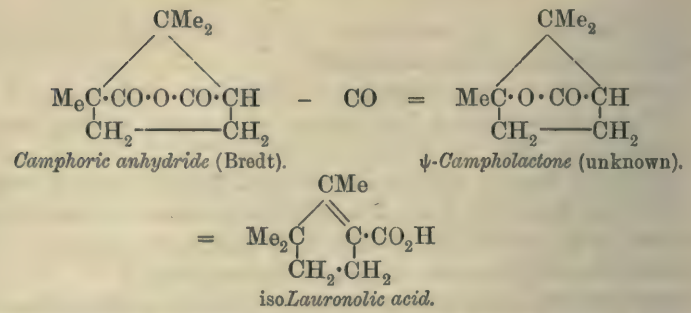
In endeavouring to obtain further evidence as to the probable constitution of these substances, it may be noted, in the first place, that *iso*lauronolic acid and the oily lactone mixture, $C_9H_{14}O_2$, are formed from camphoric anhydride by the removal of carbon monoxide:

$$2C_{10}H_{14}O_3 = \underset{\text{iso}\textit{Lauronolic acid.}}{C_9H_{14}O_2} + \underset{\textit{Oily lactones.}}{C_9H_{14}O_2} + 2CO.$$

If, then, we assume that the formula suggested by Bredt for camphoric acid is correct,† there can be scarcely any doubt that the conversion of camphoric anhydride into *iso*lauronolic acid must be represented thus:

* In the preliminary account of this work in the Proceedings (*loc. cit.*) we suggested that the lactone might, on further investigation, prove to be the lacton of hydroxyhexahydro-xylic acid.

† The reasons for adopting this formula will be discussed in a future paper.

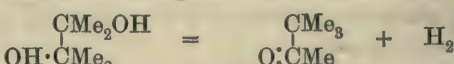


Camphoric anhydride (Bredt). *ψ-Campholactone* (unknown).

iso*Lauronolic acid.*

The isomeric change of *ψ*-campholactone into *iso*lauronolic acid necessitates the assumption of the migration of a methyl group from one carbon atom to the adjacent one; a change which is not unknown, as Dr. Lapworth pointed out in his paper, "On the Constitution of Camphor," at the Bradford meeting of the British Association.

Thus the transformation of *pinacone* into *pinacolin*,



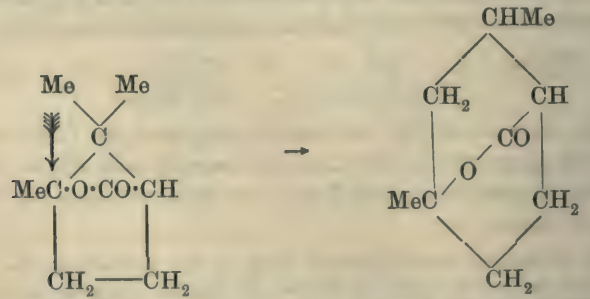
and of *pinacolyl alcohol* into *tetramethylethylene*,



affords examples of an exactly similar migration of a methyl group. Very probably, isomeric changes of this nature will be found to take place frequently in the camphor group.

The formation of the lactones of hydroxyhexahydro-xylic acid during the action of aluminium chloride on camphoric anhydride is evidently a process of a different nature.

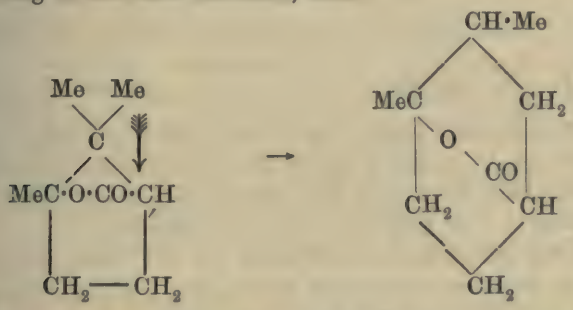
Apparently, the first stage is the same as that represented above in the case of *iso*lauronolic acid: the subsequent intramolecular change of the intermediate substance—*ψ*-campholactone—into a derivative of xylic acid may then be represented thus:



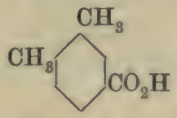
ψ-Campholactone. *Lactone of hydroxyhexahydro-xylic acid.*

In this case, one methyl of the $>CMe_2$ group enters the ring, and thus converts the original 5-membered ring into a 6-membered ring, a kind of isomeric change which has frequently been met with in the camphor series.

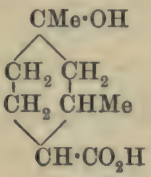
It may be noted at this stage that the formation of the lactones by the introduction of a methyl group into the ring can only take place in the way represented above, because if the methyl group were to enter the ring in the other direction, thus :



a lactone would be formed which is not a derivative of xylic acid, but of p-*xylic acid*.



If, then, the hydroxy-acids melting at 113° and 160° are hydroxy-hexahydro-xylic acids of the constitution

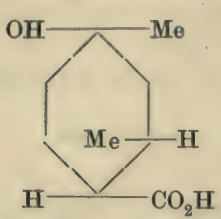


it would naturally be expected that, being δ-hydroxy-acids, they would *readily* form lactones, but this was not found to be the case, since aqueous solutions of these acids may be boiled for a considerable time without, apparently, a trace of lactone being formed.

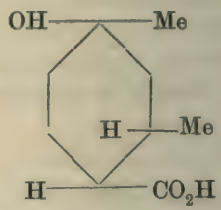
When, however, the acids are distilled, elimination of water takes place quantitatively, and two lactones are obtained ; that from the acid melting at 113° being crystalline and melting at 44°, whereas the lactone from the acid of melting point 160° is an oil.

Furthermore, these lactones on hydrolysis with baryta are reconverted into the acids from which they were obtained, showing that they are actually the lactones of these acids, and that no stereoisomeric

change has taken place at the high temperature of the distillation. Owing to the difficulty of lactone formation, we are inclined to believe that the two hydroxy-acids are the *trans*-modifications of hydroxyhexahydro-xylic acid,



and



but until the corresponding *cis*-modifications have been isolated this view must remain doubtful, and in the meantime we propose to name the hydroxy-acid melting at 160° *A-hydroxyhexahydro-xylic acid*, and that melting at 113° *B-hydroxyhexahydro-xylic acid*.

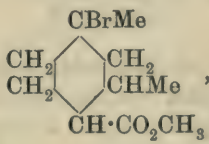
When the mixed lactones obtained by the action of aluminium chloride on camphoric anhydride are treated with phosphorus pentabromide and the product poured into methyl alcohol, a heavy oil is formed, which on fractionating yields a bromomethyl ester, $C_8H_{14}Br\cdot CO_2Me$, boiling at 165° under 30 mm., and a methyl ester, $C_8H_{13}\cdot CO_2Me$, boiling at 210° under 733 mm. pressure, the latter being formed by the elimination of hydrogen bromide from the former:

$$C_8H_{14}\begin{cases}CO\\O\end{cases} + PBr_5 = C_8H_{14}\begin{cases}COBr\\Br\end{cases} + POBr_3,$$

$$C_8H_{14}\begin{cases}COBr\\Br\end{cases} + CH_3\cdot OH = C_8H_{14}\begin{cases}CO_2CH_3\\Br\end{cases} + HBr,$$

$$C_8H_{14}Br\cdot CO_2CH_3 = C_8H_{13}\cdot CO_2CH_3 + HBr.$$

The former of these is *methyl bromohexahydro-xylate*,

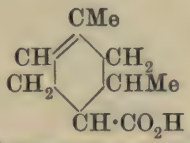


and the latter substance, which may be obtained almost quantitatively by digesting the bromomethyl ester with diethylaniline, is *methyl tetrahydro-xylate*. On hydrolysis, methyl tetrahydro-xylate yields the corresponding *tetrahydro-xylic acid*, a colourless, crystalline substance which melts at about 72°, and shows all the properties of an unsaturated acid. So far, it has not been found possible to definitely assign a constitutional formula to this new acid, since the elimination of

hydrogen bromide from bromohexahydro-xylic acid may take place in two directions, giving the following acids:



Δ^4-*Tetrahydro-xylic acid.*



Δ^3-*Tetrahydro-xylic acid.*

Besides this tetrahydro-xylic acid of melting point 72°, which we have reason to believe corresponds to the hydroxy-acid melting at 160°, there is also formed, when the methyl tetrahydro-xylate mentioned above is hydrolysed, a second tetrahydro-xylic acid, which perhaps corresponds to the hydroxy-acid melting at 113°.

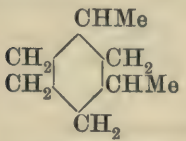
This acid has, so far, only been obtained as an oil, probably because it could not be entirely freed from the tetrahydro-xylic acid of melting point 72°; when obtained in a pure state, it will very likely be found to be crystalline.

One of the most remarkable properties of tetrahydro-xylic acid (m. p. 72°) is the ease with which it is converted into xylic acid on treatment with sulphuric acid; as this change not only takes place very readily at 70—80°, but even at the ordinary temperature, sulphur dioxide is slowly evolved, and after standing for 4 weeks, it is found that a quantity of xylic acid has been produced, a transformation which seems to us to be very strong evidence in support of our contention that this acid is a tetrahydro-xylic acid.

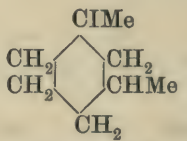
In order, however, to obtain still more positive confirmation of our view that the substances described in this paper are derivatives of xylic acid, a number of experiments were instituted on the reduction of the mixed lactones with hydriodic acid, with results which, although not so decisive as could have been wished, nevertheless point in the same direction. When the mixed lactones are heated with fuming hydriodic acid at 180°, reduction readily takes place, and the product is found to consist of a *hydrocarbon*, C_8H_{16}, of boiling point 119°; an *iodide*, $C_8H_{15}I$, boiling at 115° under 32 mm. pressure, and an *acid*, $C_8H_{15}\cdot CO_2H$, which boils at 248—253°.

The hydrocarbon is evidently *hexahydro*-m-*xylene* and identical with the substance of this constitution which has already been obtained by heating camphoric acid at 280° with hydriodic acid and in other ways (see p. 349), the iodide is probably *iodohexahydro*-m-*xylene* [1 : 1 : 3] and isomeric with the *iodohexahydro*-m-*xylene* [1 : 3 : 5] of Knoevenagel (see p. 349) and the acid is doubtless a mixture of the stereoisomerides of *hexahydro-xylic acid*, but the small yield produced during this reduction has not, so far, allowed of our separating these isomerides.

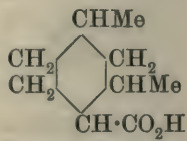
The constitution of these products of the action of hydriodic acid on the mixed lactones is readily understood from the following formulæ:



*Hexahydro-*m*-xylene.*



Iodohexahydro-m-xylene (1 : 1 : 3).



Hexahydro-xylic acid.

and their formation is undoubtedly confirmatory evidence of our view that the compounds described in this paper are derivatives of xylic acid. As so much of the material used in these experiments with hydriodic acid was converted into neutral substances, we next tried to reduce a large quantity of the mixed tetrahydro-xylic acids as they are obtained by the hydrolysis of the methyl tetrahydro-xylate mentioned on page 352, but although we used sodium and boiling amyl alcohol as the reducing agent, and carried out the operation four times with the same material, only about 5 per cent. of the unsaturated acid was reduced, yielding an oily acid, $C_8H_{15}\cdot CO_2H$, which again doubtless consisted of a mixture of the stereoisomeric modifications of hexahydro-xylic acid.

In the preparation of *iso*lauronolic acid and the mixed lactones of hydroxyhexahydro-xylic acid by the action of aluminium chloride on camphoric anhydride, the process is complete in a few hours, and the product was usually worked up after standing for 15 hours. On one occasion, however, the mixture was allowed to remain in a cool place for four weeks, when, on treating the product in the usual way, about the same quantity of the mixed lactones was obtained, although, curiously enough, the *iso*lauronolic acid, which must have been present at first, had almost entirely disappeared.

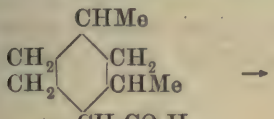
In the place of this acid, a quantity of a liquid acid was obtained which boiled constantly at 155° under 30 mm. pressure and consisted principally of a saturated acid, $C_8H_{15}\cdot CO_2H$, mixed with varying quantities of an unsaturated acid, which was apparently tetrahydro-xylic acid.

After removing the unsaturated acid by oxidation and exposing the distilled saturated acid to a low temperature, crystals melting at 75° separated, and these on examination were found to consist of the modification of hexahydro-xylic acid which Bentley and Perkin obtained by the direct reduction of xylic acid (Trans., 1897, 71, 173). The proof of this was obtained in the following way.

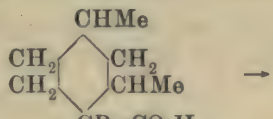
The crystals were treated with bromine and phosphorus trichloride and the product poured into methyl alcohol, when *methyl*

α-bromohexahydro-xylate was obtained as a colourless oil boiling at 143—146° under 35 mm. pressure. This, when hydrolysed with excess of alcoholic potash, yields an acid melting at 106°, which is identical with the tetrahydro-xylic acid obtained by Bentley and Perkin (*loc. cit.*)* by the reduction of xylic acid with sodium and amyl alcohol, as a direct comparison of the two specimens clearly showed.

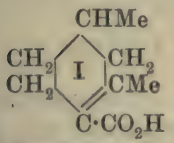
From its method of formation, this tetrahydro-xylic acid may have two formulæ, as will be seen from the following :



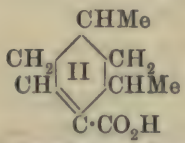
Hexahydro-xylic acid.



α-Bromohexahydro-xylic acid.



Δ^6-*Tetrahydro-xylic acid.*



Δ^1-*Tetrahydro-xylic acid.*

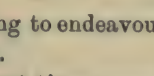
At this stage of our experiments, it is not possible to definitely decide between these two formulæ, but the behaviour of the acid with bromine, and especially on oxidation with permanganate, has led us to the conclusion that it is Δ^6-tetrahydro-xylic acid and has the constitution represented by formula I.

Since, then, it is proved that *iso*lauronolic acid, on long contact with aluminium chloride under the conditions described on p. 356, is converted into hexahydro-xylic acid—a process not only of molecular change but also of reduction,

$$\underset{\text{iso}\textit{Lauronoli acid.}}{C_8H_{13}\cdot CO_2H} + 2H = \underset{\textit{Hexahydro-xylic acid.}}{C_8H_{15}\cdot CO_2H}$$

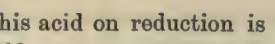
it is obviously interesting to endeavour to understand how this remarkable change takes place.

There is, at the present time, scarcely any doubt that the constitution of *iso*lauronolic acid is represented by the formula



* The melting point, 103°, given by Bentley and Perkin for this acid is too low ; it should be 106°.

and it is known that this acid on reduction is readily converted into dihydro*iso*lauronolic acid,



If now we compare this last formula with that of hexahydro-xylic acid, we see, at once, that in order to produce the latter from the former it is only necessary for one methyl of the $>CMe_2$ group to migrate into the ring, and thus convert the 5-membered ring of dihydro*iso*lauronolic acid into the 6-membered ring of hexahydro-xylic acid, a change similar to that referred to on p. 334 in discussing the formation of the lactone of hydroxyhexahydro-xylic acid:



*Dihydro*isolauronolic acid. *Hexahydro-xylic acid.*

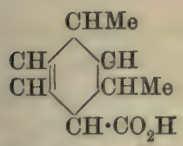
It has already been mentioned that tetrahydro-xylic acid (m.p. 107°) was first obtained by Bentley and Perkin (*loc. cit.*) by reducing xylic acid, dissolved in boiling amyl alcohol with sodium, and now that this acid has been obtained by the hydrolysis of methyl-*a*-bromohexahydro-xylate, and it has thus been proved that the double bond must be attached to the same carbon atom as the carboxyl group, interesting evidence is obtained as to the course which the reduction of xylic acid follows under the conditions mentioned above.

Aschan (*Ber.*, 1891, **24**, 1865; *Annalen*, 1892, **271**, 234) has shown that benzoic acid on reduction with sodium amalgam is first converted into Δ^2-tetrahydrobenzoic acid, and that this acid on boiling with strong alkalis undergoes isomeric change into Δ^1-tetrahydrobenzoic acid:

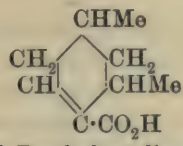


Δ^2-*Tetrahydrobenzoic acid.* Δ^1-*Tetrahydrobenzoic acid.*

In the case of xylic acid, the reduction would be expected to pursue a similar course, yielding in the first place Δ^2-tetrahydro-xylic acid, which then would be converted into the Δ^1-acid by boiling with alkali.



Δ^2-*Tetrahydro-xylic acid.*



Δ^1-*Tetrahydro-xylic acid.*

Since, however, in the experiments of Bentley and Perkin on the reduction of xylic acid, sodium and boiling amyl alcohol were employed, both reduction and the isomeric change from Δ^2 to Δ^1 would be expected to take place simultaneously, and it is therefore easy to understand that Δ^1-tetrahydro-xylic acid was the acid actually obtained.

Experimental.

The Action of Aluminium Chloride on Camphoric Anhydride. Preparation of iso*Lauronolic Acid and of the Mixed Lactones of Hydroxyhexahydro-xylic Acid.*

In studying this reaction, a very large number of experiments were made, principally with the view to determining the conditions which give the largest yield of the lactones, and as the result of these we ultimately adopted the following method.

Carefully dried camphoric anhydride (100 grams) is dissolved in pure dry chloroform (400 c.c.) in a flask fitted with a cork through which a long tube passes, in order that the gases produced during the subsequent reaction may be led away through the draught-hole of the draught-cupboard or into the open air. One hundred grams of the best aluminium chloride prepared from aluminium * is then added, when in a short time a vigorous reaction commences, accompanied by the evolution of carbon monoxide and hydrogen chloride, but as no great rise of temperature takes place, it was rarely necessary to cool the flask, this being only done when the temperature rose above about 45°. After about 15 minutes, the decomposition becomes much quieter, and it is curious that there always seems to be a slight absorption of heat towards the end of the reaction.

The whole mass is allowed to stand overnight, and then mixed with $1\frac{1}{2}$ litres of water, when large quantities of aluminium hydroxide are precipitated; strong potash solution is now added until the precipitate has been completely dissolved, and the chloroform layer containing the lactones separated from the alkaline solution which contains the *iso*lauronolic acid. The aqueous solution is extracted once with chloroform, and the combined chloroform solutions washed three

* The quality of the aluminium chloride seems to have a very marked influence on the course of the reaction; we obtained our supply from Kahlbaum in sealed tubes of 100 grams.

times with water, dried over calcium chloride, and the chloroform distilled off, when a light brown oil is obtained which, on fractionation under reduced pressure (50 mm.), distils almost completely at 164—170°, and on refractionation almost the whole boils constantly at 164—166° under the same pressure. Two different preparations were analysed with the following results:

0·1940 gave 0·4960 CO_2 and 0·1578 H_2O. C = 69·7; H = 9·0.
0·1732 „ 0·4447 CO_2 „ 0·1419 H_2O. C = 70·0; H = 9·1.
$C_9H_{14}O_2$ requires C = 70·1; H = 9·1 per cent.

This oil, which is a mixture of the lactones of two of the modifications of *hydroxyhexahydro-xylic acid* (see p. 344), has a peculiar sweet smell, and distils under the ordinary pressure at 260° as a colourless oil which on standing becomes brown. It is insoluble in sodium carbonate and in caustic potash solution in the cold, but dissolves easily in the latter on warming, and the solution gives no precipitate on acidifying in the cold, but, on boiling, oily drops of a lactone soon separate. The lactone is volatile in steam, and somewhat soluble in water. The density, refraction, and magnetic rotation of the oil boiling at 164—166° (50 mm.) were determined before it was known that it was a mixture of stereoisomeric modifications, and we give these numbers because the stereoisomerism may have little effect on refraction and magnetic rotation, and the numbers may therefore still be valuable.

Density determinations: d 4°/4° = 1·0652; d 10°/10° = 1·0606; d 15°/15° = 1·0571; d 20°/20° = 1·0538; d 25°/25° = 1·0512.

Magnetic rotation.

t.	Sp. rotation.	Mol. rotation.
15·6°	1·0128	8·200

Refractive power.

d 18·5°/4° = 1·05327.

	μ 18·5°.	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$.
H^{α}	1·4692	0·44547	68·603
H^{β}	1·47760	0·45345	69·831
H^{γ}	1·48254	0·45814	70·553

The specimens examined had a slight permanent rotation equal to about − 2° for a length of 102 mm.

Several experiments on the oxidation of the oily lactone were made, but with very unsatisfactory results. When dissolved in dilute potash and treated at the ordinary temperature with daily additions

of small quantities of permanganate, oxidation takes place slowly, and after three weeks, when the action had become very sluggish, the product on examination was found to contain, besides large quantities of oxalic acid, an oily ketonic acid, which, however, was produced in such small quantity that we were unable to purify it.

Isolation and Purification of iso*Lauronolic Acid.*—As stated in a previous paper (Trans., 1898, 73, 801), the most convenient way of preparing *iso*lauronolic acid in quantity, is by treating camphoric anhydride with aluminium chloride, and several kilos. of this acid have been prepared by this method for experiments on the investigation of its constitution.

The best way to isolate the acid from the strongly alkaline extract which had been separated from the chloroform solution of the lactones, as explained on p. 341, is as follows.

After every trace of chloroform has been removed by a current of air, the clear solution is mixed with an excess of hydrochloric acid, when an ochre-coloured precipitate is thrown down, which, although somewhat sticky at first, should, on standing, become quite hard. This precipitate is dissolved in ammonia and submitted to distillation in steam, by which means the ammonium salt of *iso*lauronolic acid is dissociated, and the acid distils with the steam and ammonia.

The distillate deposits, on acidifying, a white, flocculent precipitate which melts at 127—132°, and consists of almost pure *iso*lauronolic acid, and two crystallisations from dilute acetic acid raises the melting point to 133—134°, the correct melting point of the acid.

This method of purification has been found much more convenient than that recommended by Blanc, which consists in separating the crude mixture of acids formed in the reaction by recrystallisation from alcohol. The yield of *iso*lauronolic acid obtained by the above process is from 40—50 per cent. of the camphoric anhydride employed.

After all the *iso*lauronolic acid has distilled over with the steam in the way described above, the distillation flask contains a thick oil, which, as the liquid cools, solidifies to a hard, brown button; this generally adheres firmly to the side of the flask, and on acidifying the aqueous solution of the undissociated ammonium salt, a quantity of an amorphous acid separates in white flocks. This acid is very difficult to obtain in a crystalline condition, but on one occasion the crude acid was dissolved in dilute sodium carbonate, the solution boiled with animal charcoal, and, after filtering, acidified with hydrochloric acid, when a white, amorphous precipitate was obtained, which crystallised from acetic acid in glistening needles, and melted at 255—257°. On analysis:

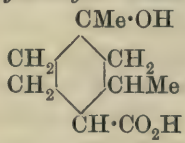
0·1584 gave 0·3911 CO_2 and 0·1196 H_2O. C = 67·3; H = 8·4.
$C_{11}H_{16}O_3$ requires C = 67·3; H = 8·2 per cent.

The *silver* salt was obtained by adding silver nitrate to a neutral solution of the ammonium salt as a white, amorphous precipitate which was very difficult to wash. On analysis:

0·2407 gave 0·3670 CO_2, 0·1090 H_2O, and 0·0885 Ag. C = 41·6; H = 5·0; Ag = 36·7.
$C_{11}H_{15}O_3Ag$ requires C = 43·5; H = 4·9; Ag = 35·7 per cent.

We were not able to repeat the preparation and analysis of this silver salt, and cannot, therefore, be sure that this well characterised acid really has the constitution $C_{11}H_{16}O_3$. The acid, which may be formed by the chloroform reacting with the camphoric anhydride in the presence of the aluminium chloride, contains no chlorine; it is readily oxidised by nitric acid, and its solution in sodium carbonate at once decolorises permanganate.

The Hydroxyhexahydro-xylic Acids and their Lactones,



When the mixed lactones obtained by the action of aluminium chloride on camphoric anhydride are heated on the water-bath with excess of baryta water, the oily drops rapidly dissolve with formation of the barium salts of the corresponding hydroxy-acids. If the excess of baryta is removed by passing carbon dioxide through the boiling liquid, and, after filtering, the filtrate is evaporated on the water-bath, a thick, syrupy barium salt is obtained which even on long standing shows no signs of crystallising. The syrupy salt was dissolved in a little water, acidified with a slight excess of hydrochloric acid, and the hydroxy-acids, which separated as a thick, pale yellow oil, extracted with pure ether. After drying over calcium chloride, the bulk of the ether was distilled off, the remainder being removed by aspirating dry air through the solution, and in this way all rise of temperature above 40° was avoided. The resulting thick syrup, after standing for some weeks in a cold place, deposited a considerable quantity of crystals, which were collected on the pump and left in contact with porous porcelain until free from oil.* The colourless

* This oil still contains considerable quantities of the mixed hydroxy-acids, A and B, along with other substances, a description of which is reserved for a future paper.

crystals thus obtained consist of the A-hydroxy-acid (m. p. 160°) mixed with varying quantities of the B-hydroxy-acid (m. p. 113°), and these two acids may be separated by dissolving in pure dry ether, evaporating to a small bulk, and allowing to stand, when a crystalline crust of the A-acid rapidly separates often in an almost pure state, the B-acid, which is much more soluble, remaining in the mother liquor. By repeating the crystallisation, the A-acid is very easily obtained in a pure condition. On analysis:

0·1546 gave 0·3554 CO_2 and 0·1308 H_2O. C = 62·7; H = 9·4.
0·1393 „ 0·3204 CO_2 „ 0·1170 H_2O. C = 62·7; H = 9·3.
$C_9H_{16}O_3$ requires C = 62·8; H = 9·3 per cent.

A-hydroxyhexahydro-xylic acid melts at 160° without decomposition. It is moderately soluble in hot, but sparingly so in cold water, and is very sparingly soluble in pure, dry ether.

It crystallises very well from water in the form of feathery leaf-like plates.

It dissolves readily in sodium hydrogen carbonate and the solution does not decolorise permanganate, except on long standing.

The *silver* salt, $C_8H_{14}(OH)\cdot CO_2Ag$, obtained on adding silver nitrate to a neutral solution of the ammonium salt, was a white, gelatinous precipitate which, on warming, became granular and was easily washed On analysis:

0·2031 gave 0·0777 gram Ag. Ag = 38·3.
$C_9H_{15}O_3Ag$ requires Ag = 38·6 per cent.

A neutral solution of the ammonium salt gives no precipitate with either barium or calcium chlorides; with copper sulphate, no precipitate is produced in the cold, but on warming, a sparingly soluble pale blue copper salt separates.

Lactone of A-Hydroxyhexahydro-xylic acid, $C_8H_{14}<\begin{matrix}O\\CO\end{matrix}$.—In order to determine whether the A-hydroxy-acid readily yielded a lactone, 2 grams were dissolved in water and subjected to rapid distillation in steam for 1 hour. The distillate, on saturating with ammonium sulphate and repeatedly extracting with ether, did not yield even a trace of lactone, and on evaporating the residue in the distilling flask to a small bulk and allowing to stand for a few days, nearly the whole of the unchanged acid separated in colourless crystals, showing that under these conditions the A-hydroxy-acid does not yield a lactone. Further experiments showed, however, that this lactone is readily obtained by simply distilling the hydroxy-acid. About 5 grams of the pure dry acid were introduced into a small fractionating flask and gently heated until the elimination of water, which commences at

about 175°, was complete; the temperature was then raised, when practically the whole of the residue distilled at 260—263° as a colourless oil. This oil was dissolved in ether, the ethereal solution washed with sodium carbonate to remove a small quantity of an acid substance which was present, dried over calcium chloride, evaporated, and the residue rapidly distilled, when almost the whole quantity passed over at 261—262° under 748 mm. pressure. On analysis:

0·2143 gave 0·5456 CO_2 and 0·1806 H_2O. C = 69·4; H = 9·4.
0·1783 „ 0·4575 CO_2 „ 0·1480 H_2O. C = 69·9; H = 9·2.
$C_9H_{14}O_2$ requires C = 70·1; H = 9·1 per cent.

The *lactone* of *A-hydroxyhexahydro-xylic acid* is a colourless oil which, when cooled in a freezing mixture, showed no signs of crystallising. That it is really the lactone of the A-hydroxy-acid and that no isomeric change had taken place at the high temperature of the distillation is shown by the following experiment. About 2 grams of the lactone were warmed with baryta water until dissolved, the well-cooled solution was then acidified with hydrochloric acid, and extracted several times with pure ether. After carefully drying with calcium chloride and evaporating to a small bulk, the ethereal solution deposited a crust of colourless crystals which melted at 160°, and on examination were found to consist of the pure A-hydroxy-acid.

B-Hydroxyhexahydro-xylic Acid.—The ether mother liquors from the purification of the A-hydroxy-acid (p. 345) yield, on concentrating, several crops of crystals consisting of the B-acid mixed with varying quantities of the A-acid, and by a long series of fractional crystallisations it is ultimately possible to obtain the much more readily soluble B-acid in a state of purity. On analysis:

0·1355 gave 0·3110 CO_2 and 0·1132 H_2O. C = 62·6; H = 9·3.
0·1490 „ 0·3426 CO_2 „ 0·1254 H_2O. C = 62·7; H = 9·3..
$C_9H_{16}O_3$ requires C = 62·8; H = 9·3 per cent.

B-Hydroxyhexahydro-xylic acid melts at 113°, but the presence of traces of the A-acid frequently lowers the melting point to 109—110°. It is much more readily soluble in water than the A-acid, and its aqueous solution on slowly evaporating over sulphuric acid deposits the hydroxy-acid in hard prisms, closely resembling crystals of cane sugar, and quite different in appearance from the leafy crystals of the A-acid.

The moderately dilute solution of the ammonium salt gives no precipitate with silver nitrate at first, but, on standing, gelatinous flocks gradually separate in small quantities. These were filtered off, and the solution concentrated on the water-bath, when after filtering from a few brown flocks, the filtrate on cooling set to a colourless jelly,

and all attempts to wash this and thus obtain the silver salt in a pure condition were unavailing.

In other respects, the neutral solution of the ammonium salt shows a similar behaviour with reagents to that of the A-hydroxy-acid.

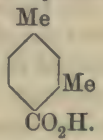
Lactone of B-Hydroxyhexahydro-xylic Acid.—As in the case of the A-hydroxy-acid, we first experimented with the view of determining whether the B-hydroxy-acid is converted into its lactone by boiling with water. The pure B-hydroxy-acid (2 grams) was dissolved in water and the solution distilled in steam for 1 hour, exactly as described in the case of the A-hydroxy-acid (p. 345). The distillate, on extraction with ether, did not yield any lactone, and from the residue in the distilling flask nearly the whole of the B-hydroxy-acid was recovered unchanged. It is therefore evident that this acid is not converted into its lactone on boiling with water. The lactone may, however, be obtained almost quantitatively by distilling the pure B-hydroxy-acid exactly as described in the case of the A-acid (p. 346). The distillate was dissolved in ether and extracted repeatedly with sodium carbonate. The ethereal solution was then dried and evaporated, and the residual oil carefully fractionated. After two distillations, almost the whole quantity passed over at 260° under 758 mm. pressure as a colourless oil which, on cooling and rubbing with a glass rod, solidified completely to a hard mass of crystals melting at 38—40°. This lactone is sparingly soluble in light petroleum, and if the solution is allowed to evaporate spontaneously, feathery groups are gradually formed which melt at 44°, and consist of the pure lactone of the B-hydroxy-acid. On analysis:

0·1850 gave 0·4755 CO_2 and 0·1528 H_2O. C = 70·1 ; H = 9·2.

$C_9H_{14}O_2$ requires C = 70·1 ; H = 9·1 per cent.

That this substance is the *lactone* of *B-hydroxyhexahydro-xylic acid*, is proved by the fact that when hydrolysed with baryta a hydroxy-acid is produced which, after extraction with ether and evaporation to a small bulk, is deposited in hard crystals which melt at 110—112°, and show all the properties of the B-hydroxy-acid.

Action of Sulphuric Acid on the Lactones of the Hydrohexahydro-xylic Acids. Formation of Xylic Acid,



It has already been mentioned in the introduction to this paper that the mixed lactones when heated with sulphuric acid are rapidly

oxidised with formation of xylic acid, and the actual experiment was carried out as follows.

The mixed lactones (5 grams) were dissolved in concentrated sulphuric acid (50 grams) and warmed in a water-bath the temperature of which was kept at between 80° and 85°. In a short time, the solution began to darken in colour, and there was much effervescence due to the escape of sulphur dioxide; when this had ceased, which was usually the case after about 10 minutes heating, the dark brown liquid was cooled and poured into three times its volume of water. After well stirring and allowing to stand overnight, the greyish coloured sandy precipitate was collected, dried, and rapidly distilled from a small retort. The crystalline distillate was dissolved in sodium carbonate, the solution boiled with animal charcoal, filtered, and the hot filtrate acidified, when an almost colourless, crystalline precipitate was thrown down which consisted of nearly pure xylic acid. After crystallising from dilute acetic acid, the substance was obtained as a colourless crystalline powder which melted at 126°. On analysis:

0·1600 gave 0·4220 CO_2 and 0·0984 H_2O. C = 71·9; H = 6·8.
0·1620 „ 0·4261 CO_2 „ 0·0976 H_2O. C = 71·7; H = 6·7.
$C_9H_{10}O_2$ requires C = 72·0; H = 6·7 per cent.

Some of this acid was intimately mixed with an equal quantity of pure xylic acid prepared from ψ-cumene, without any alteration in the melting point being produced, a proof that the two acids were identical. In order, however, to be certain of this, a quantity of the acid was converted into the *anilide*, which, after crystallising from light petroleum (b. p. 80—100°), melted at 140—141°. On analysis:

0·0763 gave 4·3 c.c. nitrogen at 18° and 757 mm. N = 6·4.
$C_{15}H_{15}ON$ requires N = 6·2 per cent.

A direct comparison of this anilide with a specimen of the anilide of xylic acid showed that the two specimens were identical.

Action of Hydriodic Acid on the Lactones of Hydroxyhexahydro-xylic Acid.

In order to determine whether it was possible to reduce these lactones directly to hexahydro-xylic acid, 25 grams of the mixed lactones were heated with 100 grams of fuming hydriodic acid (sp. gr. 1·96) and a little amorphous phosphorus in sealed tubes at 180° for 3 hours. There was much pressure in the tubes and on pouring the contents, which were highly coloured with iodine, into dilute sulphurous acid, a heavy oil separated and was extracted with ether. The ethereal solution was repeatedly washed with small quantities of dilute potash, dried over calcium chloride, and evaporated, when a colourless oil remained which smelt strongly of hexyl iodide.

This oil was distilled from a fractionating flask, at first under the ordinary pressure, when a quantity of oil came over below 150°; the residue, which was fractionated under reduced pressure (20 mm.) distilled at 110—120°, leaving a slight residue smelling of phosphorus compounds. The first portion on repeated fractionation distilled constantly at 119°, but contained traces of iodine; it was therefore digested with sodium and again distilled, when the whole passed over at 119°, under 760 mm. pressure, but still contained faint traces of iodine. On analysis:

0·1785 gave 0·5569 CO_2 and 0·2273 H_2O. C = 85·1; H = 14·2.

The substance was again distilled over sodium and was now free from iodine. On analysis:

0·1610 gave 0·5042 CO_2 and 0·2056 H_2O. C = 85·4; H = 14·2.
C_8H_{16} requires C = 85·71; H = 14·3 per cent.

This hydrocarbon is saturated, since it does not decolorise permanganate and is not attacked by bromine at the ordinary temperature.

A careful comparison of the properties of this hydrocarbon with those of known saturated hydrocarbons of the formula C_8H_{16} leads at once to the conclusion that it is *hexahydro*-m-*xylene*. This hydrocarbon has been obtained by heating camphoric acid at 280° with hydriodic acid (Wreden, *Annalen*, 1877, 187, 155), and also from heptanaphthenecarboxylic acid by similar treatment (O. Aschan, *Ber.*, 1891, 24, 2718), and is described as a mobile liquid boiling at 119° under 755 mm. pressure and stable towards bromine. The latter method of formation, taken in connection with the present experiments, is instructive, and indicates that it may be a common property of saturated closed chain carboxylic acids when heated with hydriodic acid to lose carbon dioxide and yield the corresponding hydrocarbon.

The oil separated from the hexahydro-*m*-xylene by fractionation under reduced pressures and boiling at 110—120° under 20° mm. pressure was twice carefully refractionated, when almost the whole distilled at 113—115° under 32 mm. pressure with elimination of a little hydrogen iodide. This oil, which rapidly became dark coloured owing to the separation of iodine, was analysed, with the following results:

0·1486 gave 0·2280 CO_2 and 0·0923 H_2O. C = 41·84; H = 6·9.
0·2067 „ 0·1983 AgI. I = 51·81.
$C_8H_{15}I$ requires C = 40·4; H = 6·3; I = 53·36 per cent.

It is very probable that this substance is iodohexahydro-*m*-xylene [1:1:3] and isomeric with the iodohexahydro-*m*-xylene [1:3:5] boiling at 92—93° under 10 mm. pressure, which Knoevenagel (*Annalen*, 1897,

297, 163) obtained by the action of hydriodic acid on dimethyl-1 : 3-*cyclo*hexanol-5.

The alkaline liquid obtained by extracting the ethereal solution of the crude product of the reduction of the lactone with potash in the way described above gave on acidifying with hydrochloric acid and extracting with ether in the usual way, 8 grams of a thick, oily acid. On fractionating this under reduced pressure (25 mm.) about half passed over between 160° and 175°, leaving a viscid residue which contained phosphorus and did not distil until above 300°. The fraction boiling at 160—175° under 25 mm. pressure was twice distilled under the ordinary pressure and in this way 2 grams of an oil were obtained which distilled at 248—253°. On analysis:

0·1460 gave 0·3680 CO_2 and 0·1329 H_2O. C = 68·74 ; H = 10·11.

$C_9H_{16}O_2$ requires C = 69·23 ; H = 10·25.

There can scarcely be a doubt that this acid is hexahydro-xylic acid, $C_8H_{15}\cdot CO_2H$, produced by the direct reduction of the lactone.

Action of Phosphorus Pentabromide on the Lactones of the Hydroxyhexahydro-xylic Acids.

When the lactone and phosphorus pentabromide are mixed in molecular proportion, the pentabromide rapidly dissolves with considerable rise of temperature and evolution of some hydrogen bromide. If the product after standing for some time is heated for a few minutes on the water-bath and then poured into methyl alcohol, two substances are produced, namely, *methyl bromohexahydro-xylate* and *methyl tetrahydro-xylate*.

In order to isolate the product of the reaction, the methyl alcohol solution is poured into much water, the heavy oil which separates extracted with ether, the ethereal solution washed with water and dilute sodium carbonate, dried over calcium chloride, and the ether distilled off. The residual oil is then fractionated under reduced pressure (40 mm.) and thus roughly separated into two portions boiling at 120—135° and 135—180° respectively. From the latter, by repeated fractionation, a pungent smelling oil may be obtained boiling at 160—165° under 30 mm. pressure and consisting of *methyl bromohexahydro-xylate*, $C_8H_{14}Br\cdot CO_2CH_3$. On analysis:

0·3614 gave 0·2685 AgBr. Br = 31·61.

$C_{10}H_{17}O_2Br$ requires Br = 32·13 per cent.

The portion boiling at 120—135° under 40 mm. pressure was repeatedly fractionated under the ordinary pressure, and in this way a quantity of a colourless oil was obtained which contained only traces of

bromine and distilled constantly at 209—210° under 733 mm. pressure On analysis :

0·1551 gave 0·3996 CO_2 and 0·1310 H_2O. C = 70·3 ; H = 9·4.
$C_{10}H_{16}O_2$ requires C = 71·43 ; H = 9·52 per cent.

This substance is *methyl tetrahydro-xylate*, the slight deficiency in the carbon and hydrogen found being due to traces of bromine which could not be entirely removed by fractional distillation. It was subsequently obtained quite free from bromine by treating methyl bromohexahydro-xylate with diethylaniline (see below). When dissolved in chloroform, methyl tetrahydro-xylate readily absorbs bromine with the formation of *methyl dibromohexahydro-xylate*.

Methyl tetrahydro-xylate (5 grams) was dissolved in carefully dried chloroform (15 grams), and after cooling the solution below 0°, dry bromine (5 grams) dissolved in chloroform (20 grams) was slowly added, the apparatus being kept in the dark during the whole operation. The bromine was almost instantaneously absorbed and only traces of hydrogen bromide were evolved. Dry air was now drawn through the solution, cooled below 0° for some hours and until the odour of chloroform had entirely disappeared, and the viscid, light yellow oil then analysed, with the following result :

0·2541 gave 0·2762 AgBr. Br = 46·25.
$C_{10}H_{16}O_2Br_2$ requires Br = 48·8 per cent.

Methyl dibromotetrahydro-xylate, $C_8H_{13}Br_2 \cdot CO_2CH_3$, is an unstable substance which, when exposed to the air at the ordinary temperature, rapidly loses hydrogen bromide and becomes dark coloured. On leaving a small quantity over paraffin wax and sulphuric acid in an exhausted desiccator for two days, it was noticed, on opening the desiccator, that much hydrogen bromide had been formed, and the oil, on analysis, was found to contain only 42·8 per cent. of bromine.

A-Tetrahydro-xylic acid (m. p. 72°).

This acid is readily obtained by the hydrolysis of its methyl ester with alcoholic potash, and in preparing it in quantity the following method was always employed.

Methyl bromohexahydro-xylate was mixed with twice its weight of diethylaniline and the mixture heated to boiling for 6 hours ; the product, after cooling, was then poured into excess of dilute hydrochloric acid and the oil extracted with ether. The ethereal solution was repeatedly washed with dilute hydrochloric acid, to remove the last traces of diethylaniline, then with sodium carbonate, dried over calcium chloride, and the ether distilled off, when a light brown oil was obtained

which, after repeated fractional distillation, boiled constantly at 212—213° under 750 mm. pressure. On analysis:

0·1136 gave 0·2970 CO_2 and 0·0954 H_2O. C = 71·3; H = 9·3.
$C_{10}H_{16}O_2$ requires C = 71·4; H = 9·5 per cent.

The *methyl tetrahydro-xylate* thus obtained was hydrolysed by boiling with excess of methyl alcoholic potash for one hour, the product dissolved in water, evaporated until quite free from methyl alcohol and acidified with hydrochloric acid, when the tetrahydro-xylic acid was precipitated as an oil. This was extracted with ether (free from alcohol), the ethereal solution washed with water, dried over calcium chloride, and the ether distilled off, when a light brown oil was obtained which, after twice fractionating under diminished pressure, distilled constantly at 147—149° (20 mm.).* On analysis:

0·1524 gave 0·3915 CO_2 and 0·1236 H_2O. C = 70·1; H = 9·0.
$C_9H_{14}O_2$ requires C = 70·1; H = 9·1 per cent.

* The *methyl tetrahydro-xylate* obtained in this way is undoubtedly a mixture of the methyl esters of isomeric tetrahydro-xylic acids, and before this was discovered, the density, magnetic rotation, and refractive power of a very carefully fractionated sample of the oil were determined by W. H. Perkin, sen. The following is a brief statement of the results obtained:

d 10°/10° = 0·99556; d 15°/15° = 0·99181; d 20°/20° = 0·98823.

Magnetic rotation.

t = 11·5°; sp. rotation = 1·1380; mol. rotation, 10·682.

Refraction, d 15°/4° = 0·99097.

$\frac{\mu-1}{d}p$ - H_α = 79·025; H_β = 80·752; H_γ = 81·651.

The permanent rotation of this sample was −1·21° for 102 mm. = $[\alpha]_D$ = −1·195, and in the case of the sample prepared without diethylaniline, and analysed (see p. 351), the permanent rotation was found to be −1·24 for 100 mm. = $[\alpha]_D$ = −1·249.

Since it is unlikely that the magnetic rotation and refractive power of the two isomeric methyl tetrahydro-xylates would differ in any marked degree, it is interesting to compare the numbers obtained in the case of this unsaturated 6-membered ring with those of methyl *iso*lauronolate and methyl lauronolate, which are isomeric derivatives of an unsaturated 5-membered ring. The comparison is as follows:

	Mol. rotation.	$\frac{\mu-1}{d}p$ for H_α.
Methyl *iso*lauronolate	11·312	80·596
Methyl lauronolate	10·520	79·257
Methyl tetrahydro-xylate	10·682	79·025

It is certainly remarkable that whilst the numbers are so very similar in the two latter esters, they should differ so widely from those of methyl *iso*lauronolate, and further investigation may prove that there is a closer relationship between lauronolic acid and tetrahydro-xylic acid than is at present assumed to be the case. The preparation and properties of the methyl and ethyl esters of lauronolic acid will be described in a subsequent paper.

It will be seen that the analytical numbers agree exactly with those required by the formula for tetrahydro-xylic acid, and for a long time it was thought that this oily acid was a pure and single substance. However, after a considerable quantity had been left standing for some weeks in a cool place, it began to deposit crystals, and on cooling in a freezing mixture the whole became converted into a semi-solid mass which, at the ordinary temperature, liquefied again almost completely. After cooling well, the crystals were separated as far as possible from the oil by means of the pump, using a funnel surrounded by a freezing mixture, the solid mass was then left in contact with porous porcelain until quite free from oily mother liquor, and then crystallised from dilute alcohol, from which it separated in the form of glistening plates. On analysis :

0·1595 gave 0·4070 CO_2 and 0·1293 H_2O. C = 69·6 ; H = 9·0.
0·144 „ 0·3689 CO_2 „ 0·118 H_2O. C = 69·9 ; H = 9·1.
$C_9H_{14}O_2$ requires C = 70·1 ; H = 9·1 per cent.

This acid, which we propose to call *A-tetrahydro-xylic acid*, melts at about 72° when rapidly heated, but like many other similarly constituted acids, the melting point is much influenced by the rapidity of heating and by the slightest impurity. It is readily soluble in most organic solvents, but is almost insoluble in water; in a current of steam, it volatilises with great ease. In many of its properties, tetrahydro-xylic acid shows great similarity to lauronolic acid ; like the latter, it instantly reduces permanganate in cold sodium carbonate solution, and it does not appear to be reduced by boiling with amyl alcohol and sodium (compare p. 355).*

Action of Sulphuric Acid.—When tetrahydro-xylic acid is warmed with concentrated sulphuric acid at about 80°, oxidation rapidly takes place with evolution of sulphur dioxide, and on pouring the product into water a very sparingly soluble acid separates, which, after distillation and recrystallising from dilute acetic acid, melts at 126° and shows all the properties of xylic acid. On analysis :

0·1102 gave 0·2901 CO_2 and 0·0686 H_2O. C = 71·8 ; H = 6·9.
$C_9H_{10}O_2$ requires C = 72·0 ; H = 6·7 per cent.

Even when left in contact with concentrated sulphuric acid for some days at the ordinary temperature, the solution becomes brown and smells of sulphur dioxide, and on pouring into water a crystalline acid

* Experiments which have been made with the object of reducing lauronolic acid show that this acid resists the action of reducing agents in a remarkable way, and is not even affected on treatment with sodium and alcohol. In this respect, it differs from *iso*lauronolic acid, which is comparatively easily reduced to dihydro*iso*-lauronolic acid (compare footnote, p. 352).

separates which, after purification, melts at 126° and evidently consists of xylic acid.

Anilide of Tetrahydro-xylic Acid.—In order to determine whether a separation of the constituents of the oily mixture of tetrahydro-xylic acid was possible by conversion into the anilides and fractional crystallisation, 5 grams of the oily acid were digested with 15 grams of aniline for 2 days. The brown product was poured into dilute hydrochloric acid, the oily precipitate extracted with ether, the ethereal solution washed first with dilute hydrochloric acid, and then with dilute potash solution, dried with calcium chloride, and the ether distilled off. The residue quickly solidified, and, after leaving it in contact with porous porcelain for a short time, the almost colourless mass was easily purified by recrystallisation from light petroleum (b. p. 80—100°), from which it separated in satiny crystals melting at 131—132°. On analysis:

0·1930 gave 10·8 c.c. nitrogen at 24° and 761 mm. N = 6·2.

$C_{15}H_{19}ON$ requires N = 6 per cent.

This substance being the anilide of an unsaturated acid, could not be hydrolysed with strong acids, and in attempting the hydrolysis with alcoholic potash it was found that this reagent had apparently no action, as after boiling for two days almost the whole of the substance was precipitated unchanged on the addition of water. When, however, the anilide was heated in a sealed tube with strong alcoholic potash at 170° for 10 hours, some decomposition had taken place, but on evaporating off the alcohol and adding water, more than half of the unchanged anilide separated out. After filtering, the alkaline liquid was acidified and the oily acid extracted with ether in the usual way, when the ethereal solution on evaporating deposited an oil which, on standing over sulphuric acid in a vacuum, soon solidified to crystals melting at 66—68°, showing that the substance of melting point 131—132° is the *anilide* of *A-tetrahydro-xylic acid.*

In preparing the anilide in this way, any acid which had remained unchanged was extracted by shaking the ethereal solution with potash as described above. Since, then, the original oily acid was a mixture, it is evident that if, as was the case, a large proportion of A-tetrahydro-xylic acid had been removed as anilide, the remainder should consist principally of the other isomeride. The acid was isolated from the alkaline washings and fractionated, when the whole quantity passed over at 253° as a colourless oil, which became semi-solid in a freezing mixture, and behaved very much like the original acid before treatment with aniline. Apparently, then, both the isomerides are converted into anilides by boiling with aniline, but the anilide melting at 132° evidently crystallises with greater facility, and is, therefore,

more readily obtained in a state of purity. We did not carry this investigation further because, even if we had succeeded in separating the anilides by crystallisation, they are hydrolysed with such difficulty that the process could only be used, at the best, for the preparation of small quantities of the two acids.

Action of Sodium and Amyl Alcohol on the Mixed Tetrahydro-xylic Acids.—In this attempt to reduce the tetrahydro-xylic acids, 30 grams of the mixed acids, as obtained by the hydrolysis of methyl tetrahydro-xylate (p. 352), were dissolved in 2 litres of amyl alcohol in a large, round-bottomed flask connected with a wide condenser.

The solution was heated to boiling, the flame removed, and then sodium (40 grams) dropped in in three portions, and sufficiently quickly to keep the liquid boiling as rapidly as possible. As soon as the reaction had slackened, heat was applied, and when the sodium had dissolved, sufficient dilute hydrochloric acid was added to render the product distinctly acid; the alcohol layer was then separated, and distilled from a retort until the temperature rose to 120—125°. The treatment with sodium was repeated exactly as before, and four times in all, water was then added, and after the aqueous extract had been separated, the bulk of the amyl alcohol was removed by distillation and the remainder by distillation in steam. The aqueous residue in the steam distillation flask was combined with the aqueous extract, and the whole, after saturating with carbon dioxide, oxidised at 0° with permanganate, when it was found that a large amount of the oxidising agent was required before the colour remained permanent.

After standing for 1 hour at 0°, the excess of permanganate was removed by adding sodium sulphite, the whole boiled, filtered, the filtrate concentrated, acidified, and distilled in steam as long as oily drops passed over.

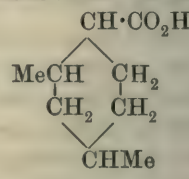
The distillate was saturated with ammonium sulphate and extracted several times with ether; the ethereal solution was then dried over calcium chloride and evaporated, when from 60 grams of tetrahydro-xylic acid about 4 grams of an oily acid were obtained, almost the whole of which, on distillation, passed over at 253—255°. On analysis:

0·1225 gave 0·3112 CO_2 and 0·1129 H_2O. C = 69·3; H = 10·2.

$C_9H_{16}O_2$ requires C = 69·2; H = 10·2 per cent.

There can scarcely be a doubt that this acid is a mixture of the stereoisomeric modifications of hexahydro-xylic acid, but it is produced in such small quantity that we were unable to effect a separation of its constituents.

The Action of Aluminium Chloride on iso*Lauronolic Acid. Formation of* cis- *and* trans-*Hexahydro-xylic Acids,*



When aluminium chloride is left in contact with a chloroform solution of camphoric anhydride for several weeks, the product of the reaction differs in a marked way from that obtained when the mixture is worked up after standing for a few hours, as described on p. 341.

The chief difference is that almost the whole of the *iso*lauronolic acid has disappeared, and in its place large quantities of the two stereoisomeric modifications of hexahydro-xylic acid are found; these must, apparently, have been produced by the long-continued action of the aluminium chloride on the *iso*lauronolic acid.

In investigating this decomposition, several quantities of the mixture of camphoric anhydride, chloroform, and aluminium chloride, prepared exactly as described on p. 341, were allowed to stand in most cases for 6 weeks, and then worked up in the same way as before. It was noticed, in the first place, that the amount of the lactones of hydroxyhexahydro-xylic acid was approximately the same as when the mixture was allowed to stand only a short time. On acidifying the potash extract, however, instead of the usual ochre-coloured, crystalline precipitate of crude *iso*lauronolic acid, an oily acid was thrown down, which, after extracting with ether and distilling off the ether, remained as a dark brown, viscid oil.

This oil was dissolved in dilute ammonia, and subjected to distillation with steam until a sample of the distillate, on acidifying, remained clear, when it was noticed that the residue in the distilling flask, after cooling, solidified to a brown button as before. The alkaline distillate was acidified and extracted with ether, and after the ethereal solution had been dried over calcium chloride and evaporated, a large quantity of a yellow oil was left, amounting to about 25 per cent. of the camphoric anhydride employed. As this oily acid was found to contain a small quantity of a neutral oil, it was dissolved in ether, the ethereal solution extracted with dilute potash, the acid reprecipitated, and after extraction fractionated under reduced pressure (28—30 mm.).

The acid began to boil at 152°, and between this temperature and 160° the whole quantity passed over as a colourless oil which, on refractionation, distilled for the most part constantly at 155—156° under the same pressure. On analysis:

0·1761 gave 0·4483 CO_2 and 0·1565 H_2O. C = 69·42 ; H = 9·9.
$C_9H_{16}O_2$ requires C = 69·23 ; H = 10·25 per cent.
$C_9H_{14}O_2$ „ C = 70·12 ; H = 9·10 „

This analysis showed that the oil which boiled so constantly was not pure, but evidently consisted of large quantities of an acid, $C_8H_{15}\cdot CO_2H$, mixed with smaller quantities of an acid, $C_8H_{13}\cdot CO_2H$, a view borne out by the fact that the oil when dissolved in sodium carbonate was capable of reducing a good deal of permanganate in the cold. In order to remove the unsaturated constituent, the whole was dissolved in sodium carbonate and, after adding ice, treated with permanganate until the colour was no longer destroyed.

The filtrate and washings from the manganese precipitate were evaporated to a small bulk, the acid reprecipitated and subjected to distillation in steam, when the residue in the distilling flask, on standing, deposited long, yellow needles of *iso*lauronic acid, showing that the unsaturated constituent of the original oil consisted, in part, at all events, of *iso*lauronolic acid.

The distillate was extracted with ether in the usual way, and the acid again fractionated, when almost the whole quantity distilled constantly at 149—150° under 20—25 mm. pressure, but as it was still not quite stable towards permanganate, the treatment with this reagent was again resorted to, with the difference that the oxidation was carried out at the ordinary temperature instead of at 0°. After this second treatment, the acid, which now contained no trace of unsaturated impurity, distilled completely at 154—157° under 30 mm. pressure as a colourless oil which, on standing, soon began to deposit crystals.

The whole was allowed to stand for 10 days in an ice chest ; the crystals were then rapidly collected on the pump, left in contact with porous porcelain until quite dry, and finally recrystallised from dilute acetic acid, from which solvent the acid separated in long, glistening needles melting at 73—75°. On analysis :

0·1396 gave 0·3525 CO_2 and 0·1276 H_2O. C = 68·9 ; H = 10·2.
0·1531 „ 0·3883 CO_2 „ 0·1410 H_2O. C = 69·2 ; H = 10·2.
$C_9H_{16}O_2$ requires C = 69·2 ; H = 10·2 per cent.

This acid is a remarkably stable substance, since it may be boiled with nitric acid for some time without being appreciably oxidised, and on cooling it crystallises out unchanged in needles which melt sharply at 75°.

The *silver* salt was precipitated on adding silver nitrate to a nearly neutral solution of the ammonium salt as a white, gelatinous mass, which, however, on stirring and warming, became crystalline. It was collected, washed well, dried at 100°, and analysed :

0·1165 gave 0·1761 CO_2, 0·0593 H_2O, and 0·0482 Ag. C = 41·2; H = 5·6; Ag = 41·3.

$C_9H_{15}O_2Ag$ requires C = 41·1; H = 5·7; Ag = 41·1 per cent.

For a long time, no clue to the constitution of this acid, of melting point 75°, could be obtained, but ultimately the investigation of its behaviour, first with bromine and then with alcoholic potash, made it probable that it was trans-*hexahydro-xylic acid.* On comparing the properties of this acid with those of a sample of hexahydro-xylic acid prepared by Bentley and Perkin (*loc. cit.*) by the reduction of xylic acid, they were found to be identical, since on mixing equal quantities of the two different preparations, no alteration could be observed in the melting point. It is clear, therefore, that one of the acids produced by the action of aluminium chloride on *iso*lauronolic acid is trans-*hexahydro-xylic acid.*

The experiment which led us to suspect the identity of this acid was the following.

The acid of melting point 75° (9 grams) was mixed carefully with the calculated quantity of phosphorus pentachloride (12 grams), and after the reaction, which commenced at once, had ceased, the mixture was heated for 15 minutes on the water-bath. Bromine (10 grams) was then added to the well cooled product, and the whole heated on the water-bath in a reflux apparatus until the colour of the bromine had disappeared and the evolution of hydrogen bromide had almost ceased. The liquid was then gradually poured into three times its volume of well cooled methyl alcohol and allowed to stand over night. On the addition of much water, a heavy, light brown oil separated which was extracted with ether, the ethereal solution was then well washed with dilute sodium carbonate, dried over calcium chloride, and the ether distilled off, when a light yellow oil (17 grams) was obtained which distilled almost completely at 143—146° under 35—38 mm. pressure. On analysis:

0·2780 gave 0·2091 AgBr. Br = 32·0.

$C_{10}H_{17}O_2Br$ requires Br = 32·1 per cent.

This substance is *methyl α-bromohexahydro-xylate,* $C_8H_{14}Br{\cdot}CO_2CH_3$, since on hydrolysis with alcoholic potash it yields *tetrahydro-xylic acid.*

The pure methyl ester was rapidly poured into a large excess of strong boiling alcoholic potash, and after the vigorous reaction had subsided the whole was boiled for 15 minutes, mixed with water, and evaporated on the water-bath with the frequent addition of water in order to ensure the removal of the last traces of alcohol. On acidifying the alkaline solution with hydrochloric acid, an oily acid separated, but this rapidly solidified; it was extracted with ether, and the ethereal solution, after drying, evaporated, when a solid residue remained

which, on distillation, passed over at 254—255° as a colourless oil solidifying almost immediately to a hard, crystalline cake. The solid mass was spread on porous porcelain to remove traces of oily impurity, and then crystallised from dilute alcohol, from which it separated in colourless needles melting sharply at 106°. On analysis:

0·1277 gave 0·3265 CO_2 and 0·1072 H_2O. C = 69·7; H = 9·3.
0·1271 „ 0·3268 CO_2 „ 0·1060 H_2O. C = 70·1; H = 9·2.
$C_9H_{14}O_2$ requires C = 70·1; H = 9·1 per cent.

This acid is identical with the *tetrahydro-xylic acid* which is produced by the reduction of xylic acid by means of sodium and amyl alcohol. In their paper on the formation of this acid, Bentley and Perkin (*loc. cit.*) give the melting point as 103°, but this is too low, since the original specimen, prepared by the reduction of xylic acid, after several times recrystallising, was found to melt at 106°.

On intimately mixing equal quantities of this latter specimen and the acid prepared from methyl bromohexahydro-xylate, there was no alteration in the melting point.

cis-*Hexahydro-xylic Acid.*—The oil separated from the crystals of *trans*-hexahydro-xylic acid in the manner described in the last section, deposited, on standing for some months in an ice chest, a further quantity of the same acid, and after filtering from the crystals the oily filtrate became semi-solid on placing in a freezing mixture of ice and salt, but rapidly and completely melted as soon as it was taken out of the freezing mixture. This behaviour suggested that the oily acid was a mixture of two isomerides and as, in spite of many experiments, a further separation by freezing was not successful, an attempt was made to effect this separation by converting the mixture of acids into the amides and subjecting these to fractional crystallisation. The oily acid (100 grams) was mixed with a slight excess of phosphorus pentachloride, in a large flask connected with a reflux apparatus and, after the vigorous action had subsided, the whole was heated in the water-bath for 15 minutes and when cold poured in a thin stream into strong aqueous ammonia (saturated below 0°).

The crystalline amides which separated were collected on the pump, washed with ammonia, dried, ground to a fine powder, and extracted with ether, by which means oily impurity was removed and a perfectly dry, crystalline mass resulted.

This amide, which had no definite melting point and was evidently a mixture, was submitted to a series of fractional crystallisations, first from much water and then from alcohol, and in this way it was separated into a sparingly soluble amide melting at 188—189° and a more soluble, and obviously less pure, fraction melting at 120—140°.

The amide melting at 188—189° was analysed, with the following results:

0·2325 gave 19·2 c.c. nitrogen at 24° and 760 mm. N = 9·2.
$C_9H_{17}ON$ requires N = 9·0 per cent.

When boiled with concentrated hydrochloric acid, this amide was hydrolysed and the oily acid which floated on the hot liquid solidified on cooling to crystals which, without further purification, melted at 72°. It is obvious, therefore, that this amide is the amide of *trans*-hexahydro-xylic acid.

The crude amide melting at 120—140° was subjected to upwards of 50 fractional crystallisations from water, and ultimately a substance was obtained which crystallised in long, slender, silky needles and melted, not quite sharply, at 140—142°. On analysis:

0·2095 gave 17 c.c. nitrogen at 20° and 754 mm. N = 9·2.
$C_9H_{17}ON$ requires N = 9·0 per cent.

This amide, which we believe to be the amide of cis-*hexahydro-xylic acid*, dissolves readily in warm concentrated hydrochloric acid, and, on boiling, decomposition soon sets in, and oily drops of the acid appear rapidly on the surface of the liquid. The acid was extracted with ether, the ethereal solution dried over calcium chloride, and after distilling off the ether the oily residue fractionated, when almost the whole quantity passed over at 250—252°. On analysis:

0·1460 gave 0·3694 CO_2 and 0·1353 H_2O. C = 69·0; H = 10·3.
$C_9H_{16}O_2$ requires C = 69·2; H = 10·2 per cent.

cis-*Hexahydro-xylic acid*, obtained in this way, is an oil which, even when cooled below −10° and stirred with a crystal of the *trans*-acid, shows no signs of crystallising. When it is remembered that all the *trans*-acid which could be separated by freezing had already been carefully removed from the oily mixture of the hexahydro-xylic acids, and that during the conversion into and subsequent fractional crystallisation of the amides a further considerable quantity of *trans*-acid was again removed, it is unlikely that the *cis*-acid which we obtained could have contained more than traces of the *trans*-acid. At the same time, we do not suggest that the *cis*-acid was quite pure, and it is therefore possible that the melting point of its amide may not be exactly that given above.

The experiments on the substances described in this paper are being continued, and it is hoped that the results will soon be ready for communication to the Society. We desire to state that much of the

very heavy expense which was necessary in carrying out these experiments has been met by repeated grants from the Royal Society.

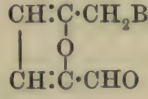
Our thanks are also due to Mr. J. Yates for undertaking the preparation of much of the material necessary for this research, and for carrying out several of the analyses.

THE OWENS COLLEGE,
MANCHESTER.

XXXVI.—*The Action of Hydrogen Bromide on Carbohydrates.*

By HENRY J. HORSTMAN FENTON, F.R.S., and MISS MILDRED GOSTLING, B.Sc.

THE authors have shown in a previous communication (Trans., 1898, 73, 554) that certain classes of carbohydrates when acted upon at the ordinary temperature with dry hydrogen bromide in ethereal solution give an intense and beautiful purple colour.* It was further shown (Trans., 1899, 75, 423) that this purple substance, when neutralised with sodium carbonate and extracted with ether, yields golden-yellow prisms of ω-bromomethylfurfural,



This reaction is produced by lævulose, sorbose, cane sugar, and inulin, an intense colour being given within an hour or two. Dextrose, maltose, milk sugar, galactose, and the polyhydric alcohols give, if anything, only insignificant colours, and these only after long standing. The authors therefore suggested that the reaction might be employed as a means of distinguishing these classes of carbohydrates, the rapid production of the purple colour being indicative of *ketohexoses*, or of substances which produce these by hydrolysis.

By relying only on the production of the purple colour, however, a mistake might possibly arise, owing to the fact that *xylose* gives

* This purple colour would appear to be due to a highly dissociable compound of ω-bromomethylfurfural with hydrogen bromide. The aldehyde gives yellow or colourless solutions in various solvents, which are turned purple by a sufficient excess of hydrogen bromide. Dilution, or addition of water, at once discharges the colour.

a somewhat similar colour after standing for a few hours. Hence, the observations should be confirmed by isolation of the crystals of bromomethylfurfural. No trace of this substance is obtained from the xylose product.

In order to identify the substance, the ether extract, after neutralisation, is allowed to evaporate to a syrup, and crystallisation promoted either by rubbing with a glass rod, or by the more certain and highly characteristic method of 'sowing' with the most minute trace of ω-bromomethylfurfural, when crystals are almost instantly formed. These are recrystallised from ether, or a mixture of ether and light petroleum, and further identified by the melting point (59·5—60·5°), and, if considered desirable, by estimation of the bromine.

It is now found, so reactive is the bromine atom in this compound, that the estimation may be accurately made by titration with silver nitrate according to Volhard's process, the crystals for this purpose being dissolved in dilute alcohol :

0·1970 gram required 10·5 c.c. *N*/10 $AgNO_3$. Br = 42·63 per cent., calculated 42·32 per cent.

This method of applying hydrogen bromide in ethereal solution is, of course, unsuitable for investigations where a higher temperature has to be employed, or where long standing is necessary, since, under such circumstances, the ether itself is attacked. Wishing to make investigations under these conditions, the authors have tried several solvents, and, at present, find that chloroform is best suited to the purpose. In each of the following experiments, 10 grams of the substance were covered with 250 c.c. of chloroform which had been saturated at 0° with dry hydrogen bromide. The mixture was contained in an accurately stoppered bottle, firmly secured with an iron clamp, and heated in a water-bath to about the boiling temperature for 2 hours. After standing for several hours, the mixture was treated with sodium carbonate (first anhydrous solid, and afterwards a few drops of strong solution), filtered, and the solution dried over calcium chloride. Most of the chloroform was then distilled off, and the remaining solution allowed to evaporate to a thick syrup in a weighed dish.

The product was then tested for ω-bromomethylfurfural by 'sowing' with the most minute trace of the substance, as described above. It was then warmed on a water-oven, kept in a vacuum desiccator over solid paraffin, and the weight estimated. When necessary, the product was recrystallised from ether, and further identified by the tests mentioned. The following results were obtained :

	Weight of crude residue.	
Swedish filter paper	3·0	crystallised at once by 'sowing,'
Ordinary cotton.....	3·3	,, ,,
Mercerised cotton	2·1	,, ,,
Straw cellulose*.....	2·3	,, ,,
Lævulose.....	2·2	,, ,,
Inulin.....	1·3	,, ,,
Potato starch.....	0·37	,, ,,
Cane sugar.....	0·85	,, ,,
Dextrose.....	0·33	uncrystallisable.
Milk sugar.....	0·37	,,
Glycogen	0·34	,,
Galactose	0·34	,,

The products from *dextrose*, *milk sugar*, and *galactose* absolutely refused to crystallise even when extracted with ether and again evaporated, or by 'sowing,' stirring, &c.

The *glycogen* product deposited a very small amount of crystalline matter on standing, but the quantity was too minute for examination; moreover, it refused altogether to crystallise in contact with the aldehyde. It may fairly be stated, therefore, that these last four substances give absolutely negative results as regards the formation of ω-bromomethylfurfural; if any is formed, its quantity is altogether too small to be detected.

The specimen of *starch* examined was freshly prepared from potato, and purified by digestion for 24 hours each with *N*/10 KOH, *N*/4 HCl, and strong alcohol; it was then washed with water and allowed to dry in the air. It will be seen that this substance gave a positive result, but that the yield was extremely small, and might yet be due to impurity. Considering the importance of the behaviour of starch, for the purpose of drawing general conclusions from these observations, it was thought advisable to make further experiments with specimens which could be relied upon, and also to investigate the behaviour of dextrin. This the authors have been enabled to do, through the kindness of Mr. C. O'Sullivan, who has placed some remarkably beautiful specimens at their disposal.

His description of the specimens is as follows:

1. Rice starch, specially purified by the permanganate method.
2. Wheat starch ,, ,, ,,

* Other forms of cellulose, likewise kindly supplied by Mr. C. F. Cross, were also examined, for example, pine-wood cellulose, and the substances separated from solution in thiocarbonate (powder and film). All of these gave good yields of ω-bromomethylfurfural.

3. Oat starch, contains traces of oil, washed with dilute KOH and dilute HCl.

4. Pea starch, first crop, washed with alkali, acid (HCl), and strong alcohol.

5. Natural dextrin, $D = 3{\cdot}87$, $[\alpha]_D = 194{\cdot}7$; $K = 0{\cdot}95$, (c 2·628).

6. α-Dextrin, C equation purified without fermentation, 30 precipitations with alcohol (Trans., 1879, 35, 772).

The examination of these specimens was conducted on a smaller scale, but under the same conditions as before, *one gram* of the substance being treated with 12·5 c.c. of the saturated chloroform solution and heated in sealed tubes for 2 hours as above. The results were as follows:

	Weight of crude residue.	
1. Rice starch	0·046	crystallised at once by 'sowing.'
2. Wheat starch	0·044	,, ,,
3. Oat starch.....	0·049	,, ,,
4. Pea starch.....	0·064	,, ,,
5. Natural dextrin	0·088	,, ,,
6. α-Dextrin	0·055	,, ,,

The results may therefore be summarised as follows. All forms of cellulose give large yields of ω-bromomethylfurfural, some varieties giving as much as 33 per cent. Lævulose, inulin, and cane sugar give yields varying from 22 to 8·5 per cent.; various starches give small yields (average about 4·5 per cent.); and dextrins 5 to 8 per cent., whereas dextrose, milk sugar, and galactose give, apparently, none at all.

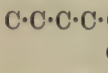
The yields represent the solid crystalline residue; this when purified by recrystallisation gives, probably, about three-quarters of its weight of pure crystals. (In the case of dextrose, &c., the yields represent the weight of syrup.)

These numbers, however, by no means represent the maximum yields obtainable, owing to the comparatively slight solubility of hydrogen bromide in chloroform. The process was conducted in the above manner only for the sake of uniform comparison. The ether method previously described gives much larger yields; for example, 12 grams of inulin treated with only 60 c.c. of the saturated ether gave 2·5 grams of substance. For the purpose of obtaining larger yields, other methods are being investigated.

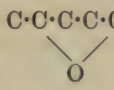
The facts recorded above, taken in conjunction with those given in our previous communications, appear to point definitely to the following general conclusions. First, that the various forms of *cellulose*

contain one or more groups or nuclei identical with that contained in *lævulose*, and that such groups constitute the main or essential part of the molecule. Secondly, that similar groupings are contained in *starches* and *dextrins*, but that the proportion of such groupings represents a relatively small part of the whole structure.

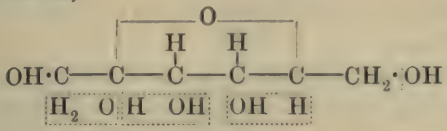
The nature of this grouping is, according to the generally accepted constitution of lævulose, the six carbon chain with a ketonic group:



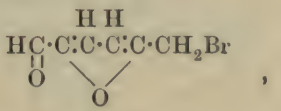
But the results might, on the other hand, be considered indicative of the anhydride or 'lacton' grouping, which Tollens suggested for lævulose:



The latter very simply represents the formation of ω-bromomethylfurfural from lævulose,*



giving



although by a little further 'manipulation' of the symbols the change could, of course, be represented by reference to the ketonic formula.

In conclusion, the authors wish to express their best thanks to Mr C. O'Sullivan for specimens of starches and dextrins, and to Mr. C. F. Cross for various samples of celluloses, also to the Government Grant Committee of the Royal Society, for funds which have enabled them to procure pure specimens of other carbohydrates.

* The change is empirically represented as

$$C_6H_{12}O_6 + HBr - 4H_2O = C_6H_5O_2Br.$$

XXXVII.—*The Ketonic Constitution of Cellulose.*

By Charles Frederick Cross and Edward John Bevan.

We are indebted to Mr. H. J. H. Fenton for a private communication of the results of his researches upon the direct condensation of a series of typical celluloses to methylfurfural, obtained in the form of the crystalline ω-bromo-derivative (Fenton and Gostling, this vol., p. 361). At the same time, these authors intimated that they did not intend to discuss in detail the problem of the constitution of cellulose, to the solution of which they contribute this important evidence. Having regard to the probability that, by these results, chemists will be attracted to the reconsideration of a matter which for long years has remained in comparative obscurity, we have deemed it opportune to collect the various items of experimental evidence available for the solution of the problem of the constitution of cellulose. For the purpose of the present discussion, we may take "cellulose" to mean the typical cotton cellulose in its bleached and purified form, and we assume, as there exists no evidence to the contrary, that it is a homogeneous substance.

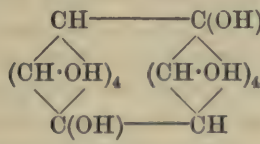
For the view that cellulose is a near analogue of starch, that is, a polyanhydride of dextrose, the evidence, when analysed, will be found to be extremely slender. The general empirical formula, $n.C_6H_{10}O_5$, is, of course, well established, but the supposed resolution, quantitatively, into dextrose groups by ultimate hydrolysis has been deduced from the somewhat superficial studies of Braconnot (*Ann. Chim. Phys.*, 1819, [ii], **12**, 172), and later of Flechsig (*Zeit. physiol. Chem.*, 1882, **7**, 523).

Nor has the matter been cleared up in regard to this essential point by the still more recent investigations of Hönig and Schubert (*Monatsh.*, 1885, **6**, 708; 1886, **7**, 455), and A. L. Stern (Trans., 1895, **67**, 74). It has been established that the first product of the action of sulphuric acid is a cellulosedisulphuric ester; that after the subsequent hydrolysis has proceeded some way, cupric-reducing groups are produced; and, finally, that dextrose may be isolated from the products (monoses) of ultimate hydrolysis. But the hydrolysis has not been studied by way of full quantitative statistics such as have been established for starch. The evidence of this process of resolution is therefore incomplete; and in any case the action of a reagent such as sulphuric acid, as compared with that of an enzyme, leaves quite open the question of attendant constitutional change. It is quite conceivable that a ketonic aggregate might undergo molecular cleavage at such points that the typical CO groups come to occupy a terminal position in the products of the change. These considerations lessen the supposed

critical value of the evidence drawn from this particular resolution of cellulose.

But there are other relationships which have been brought to light by later investigations. These we may briefly recapitulate.

The tetracetate (Cross and Bevan: "Cellulose," p. 38) is a true cellulose derivative, an ester of the unresolved molecule. The empirical formula, $C_6H_6O(OAc)_4$, is most simply expressed for the unit group as $CO{:}(CH{\cdot}OAc)_4{:}CH_2$, which implies that in the parent molecule the CO group has a ketonic position and function, and would justify the hypothesis that the aggregate might have the general form



This is not without some experimental justification, since acetates higher than the tetracetate are obtainable, which on saponification yield hydrolysed and cupric-reducing products ("Cellulose," *loc. cit.*).

Further direct evidence as to the position of the typical carbonyl, whether ketonic or aldehydic, should be afforded by a study of the acid products of oxidation. Nitric acid oxidises the celluloses to oxycelluloses (insoluble) and acids of low molecular weight, chiefly oxalic acid, tartaric acid, and a C_5 dibasic acid (Faber and Tollens, *Ber.*, 1899, **32**, 2595). *Saccharic acid, it appears, is not formed.* Further, by treatment of the oxycelluloses with lime, the products derived from the oxidised groups are dihydroxybutyric and *iso*saccharinic acid (Faber and Tollens, *loc. cit.*). In all these oxidations there is a marked absence of products with the normal C_6 chain, and the obvious interpretation of the result is that the original unit groups are of ketonic constitution. With regard to the nitric esters, we have now the results of the later investigations of Will and Lenze (*Ber.*, 1898, **31**, 68), who find that the ketoses are distinguished from the aldoses by not giving the theoretically highest nitrate. Thus lævulose and sorbinose give trinitrates, whereas dextrose and galactose give pentanitrates. In the ketoses there is an interior condensation, involving one pair of the OH groups, accompanying the ester reaction. As a secondary result, the nitrates are relatively stable. In the case of cellulose, the trinitrate (C_6) is the highest nitrate, and is obtained with difficulty. That its formation is attended by interior condensation is shown by the yields, which are notably less than those calculated for a simple ester reaction corresponding with the amount of nitrogen, that is, of $O{\cdot}NO_2$ groups in the product. These quantitative relations are much exaggerated in the nitration of the lignocellulose, in which the

ketonic type has been proved to predominate. It is to be noted that starch shows a close similarity to cellulose in regard to this reaction, with, however, a notable difference in yield. Cellulose and hydrocellulose yielded 170 per cent., but starch only 157 per cent. of nitrate, in which the total nitrogen was found to be 13·8—13·9 per cent. The CO groups may in this reaction undergo a transposition. This involves the question of the relationship of the unit C_6 groups to the complex aggregate, whether of starch or cellulose. Starch being readily hydrolysed by enzyme action, it is assumed that the ultimate products, maltose and dextrose, as constitutional groups, are represented as such in the starch molecule. We have previously dealt with the evidence in regard to the relationship of dextrose, obtained as a product of decomposition of cellulose, to the parent molecule. It must be noted here, in anticipation of the general remarks we have to make on the new evidence of Fenton and Gostling, that starch has been included in these investigations. On reference to their paper, it will be seen that starch and cellulose are widely differentiated by the new reaction, as they are in all their physiological relationships, and as they are actually in essential chemical points, although this difference has been obscured by some more obvious points of resemblance. It is an especially satisfactory feature of these new results that they place the whole "starch-cellulose" question on a sound chemical basis adequate to redirect physiological investigation. It must be confessed that the opposite procedure seldom enables a given problem to be seen in true perspective; and as we have now to call attention to the contributions of chemists to the question of starch in relation to assimilation, we may incidentally note that they establish relationships which were long overlooked by physiologists.

It had been assumed on physiological grounds that cellulose is a near analogue of starch, probably formed from it by a process of modification having rather to do with the kind or degree of molecular aggregation than any more profound constitutional change.

Brown and Morris, in their well-known paper on the subject of chlorophyllic assimilation (Trans., 1893, **63**, 604), thus express themselves: "The starch which is formed by the chloroplasts is, strictly speaking, not autocthonous, but owes its origin to antecedent cane sugar." In support of their general conclusion that cane sugar as a first product of chlorophyllic assimilation has a further direct relationship to the general nutrition of the plant, they refer to their previous investigations (Trans., 1890, **57**, 484), which showed that "of all the soluble carbohydrates examined cane sugar has the highest nutritive value." It appears from these researches that lævulose has some function complementary to that of dextrose, and it is a fair hypothesis, warranted, we think, by the present state of our knowledge,

that the ketose is more directly concerned in the elaboration of cellulose. This view is supported by some observations of A. J. Brown on the growth of the "vinegar plant" (Trans., 1886, 49, 432), communicated under the title, "On an Acetic Ferment which forms Cellulose." From this paper (p. 438) we make two extracts, which shortly present the main conclusions: (1) "The formation of cellulose by the 'vinegar plant' from the carbohydrates must not be looked upon as an act of fermentation, as it is evidently only a product of assimilation formed for the special use of the plant itself." (2) "It is evident from the experiments that . . . . . lævulose [is] far more favourable to the growth of the ferment than dextrose, and also that cellulose is formed [from it] more freely. During the growth of the ferment in lævulose solutions no trace of fermentative action was observed."

On the direct evidence thus briefly summed up, we have not hesitated to adopt as a working hypothesis the view that cellulose is of ketonic constitution. There are many points bearing indirectly on the subject, but in view of the results now disclosed by Fenton and Gostling it is unnecessary to prolong or labour a discussion based on *a priori* considerations.

These results come to us with all the greater force as confirming the evidence which has been for some time accumulating. Moreover, the polyaldose view of the constitution of cellulose has been barren of suggestion. It does not differentiate cellulose from starch; it fails to give any account of the part played by ketoses generally in plant life in the main work of building up permanent tissue; it leaves unexplained the origin of the condensed or unsaturated compounds which are the characteristic components of lignified tissue, and of the widest distribution in the plant world.

Now that we are aware of the simple condensation of cellulose, or, rather, of its constituent hexose groups, to methylfurfural, we are in possession of a many-sided clue to the main problems which we have been endeavouring largely by indirect means to solve. We defer to a later occasion their further and more specific discussion. The reaction itself is being further investigated by Fenton. Although it has been reduced to a quantitative method, giving numbers which have full comparative value, the results are considered to be yet very far short of the optimum. We must await these developments before drawing any more positive conclusions than are contained in the communication of Fenton and Gostling, strengthened by the further weight of evidence which we have collected from the somewhat scattered literature.

XXXVIII.—*Isomeric Hydrindamine Camphor-π-sulphonates. Racemisation of α-Bromocamphor.*

By Frederic Stanley Kipping, Ph.D., D.Sc., F.R.S.

On continuing the study of the compounds formed by the combination of externally compensated hydrindamine with various optically active acids (Trans., 1900, **77**, 861), one of the first salts to be examined was that prepared from *d*-camphor-π-sulphonic acid; * this compound is a simple reduction product of α-bromo- and α-chloro-camphor-sulphonic acids, both of which yield with hydrindamine the separable isomeric partially racemic salts already described, and consequently it seemed highly probable that hydrindamine camphor-π-sulphonate would be resolvable into corresponding products by fractional crystallisation.

At first, great difficulty was experienced in isolating fractions showing any difference in properties whatsoever, but after some fruitless attempts, preparations differing considerably in specific rotation were obtained.

The assumption that these different fractions represented the long-sought-for analogues of the isomeric hydrindamine bromocamphor-sulphonates, seemed to be justified in the first instance, as various preparations showed a constant difference in optical properties, but the great similarity in appearance—although not greater than in the case of the *cis*-π-camphanates—the extremely small proportion of the more sparingly soluble isomeride, its low specific rotation, and other facts aroused suspicion as to the accuracy of such a view, and further experiments showed it to be untenable.

The separation of the crude hydrindamine *d*-camphor-π-sulphonate into different fractions was ultimately proved to be due to the presence of an extremely small quantity of a salt derived from an isomeride of the *d*-acid. There were, therefore, three possibilities. The new isomeride might be (*a*) enantiomorphously related to, (*b*) optically different from, but structurally identical with, or (*c*), optically and structurally different from, *d*-camphor-π-sulphonic acid. Experiment showed that the two acids are enantiomorphously related.

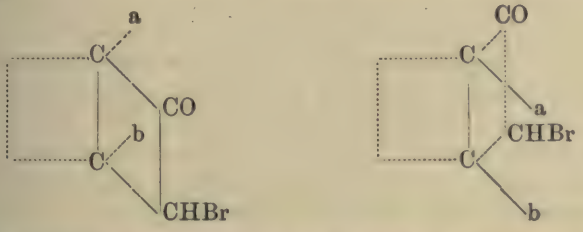
Now the *d*-acid was prepared by the reduction of purified ammonium bromocamphorsulphonate, which, in its turn, had been obtained from the product of the sulphonation of α-bromocamphor; it follows, therefore, that racemisation occurs, although to a very limited extent,

* As the SO_3H group in this acid is in the same position in the molecule as the halogen atom in π-chloro- and π-bromo-camphor (Kipping and Pope, Trans., 1895, **67**, 371), the letter π is used to distinguish this acid from the isomeride discovered by Reychler.

either during the reduction of the bromo-acid or during the sulphonation of the bromocamphor.

The optical inversion of camphor itself has already been observed by Kipping and Pope (Trans., 1897, 71, 958), who pointed out that the formation of enantiomorphously related acids on sulphonating this ketone necessitates the conclusion that during the reaction a partial racemisation takes place. It was also stated in the same paper (p. 962) that "in the case of α-bromocamphor, optical inversion does not accompany sulphonation." This statement at the time seemed to be based upon sufficient evidence, namely, the fact that, even when working with very large quantities of bromocamphorsulphonic acid and its derivatives, the presence of isomerides had never been observed. Since then, a great deal of work has been done with this acid, and the existence of optically isomeric forms has until now passed unnoticed; probably they would have long remained undiscovered had it not been that, judging by analogy, *d*-camphor-π-sulphonic acid should give isomeric, partially racemic hydrindamine salts, and large quantities of this salt were therefore examined with great care.

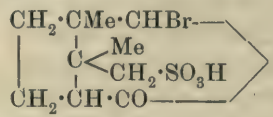
It must now be concluded, however, that the statement referred to above is incorrect, and that α-bromocamphor, like camphor, may be partially racemised during sulphonation. This, no doubt, is an extraordinary fact: as will be evident from the following diagrammatic representation, racemisation necessitates the transference—as a whole—of part of one of the closed chains from one position to another,



a change compared with which all other cases of racemisation appear to be extremely simple.

That this partial racemisation occurs during the sulphonation of the bromocamphor, and not during the reduction of the ammonium salt of the sulphonic acid, is tolerably certain; firstly, because camphor itself is racemised during sulphonation; secondly, because the conditions of the experiment and the reagents used in reducing the bromo-acid are not such as usually bring about intramolecular change (the conversion of *w*-bromocamphoric anhydride into *iso*camphoric acid on reduction being in no wise an analogous case); and thirdly, because a considera-

tion of the formula, which has previously been assigned to bromocamphorsulphonic acid (Kipping, Trans., 1896, 69, 913),



renders this conclusion the more probable.

Since the *l*-acid, which is found to be present, is enantiomorphously related to the *d*-acid, the asymmetric group, $\overset{a}{b}\!>\!C\!<\!\overset{Me}{CH_2\cdot SO_3H}$, in the former must be the antipodes of this group in the latter; consequently, if racemisation were to occur during the reduction of the bromo-acid, the group in question, as well as the closed ring, would have to undergo optical inversion, whereas if the bromocamphor itself is racemised, sulphonation alone would give the enantiomorphously related forms.*

For these reasons, which appear to be conclusive, the presence of *l*-bromocamphorsulphonic acid in the ordinary *d*-acid may be considered as established; but the quantity of this isomeride is so small that to try and isolate an externally compensated or racemic compound from the ordinary ammonium salt seemed to be a task of such difficulty, and to offer results of such small value, that it has not been attempted.

It may be pointed out, however, that the proportion of the *l*-acid may vary considerably in different preparations, depending upon the method of sulphonation and other details.

Experimental.

The camphor-π-sulphonic acid employed in these experiments was prepared by reducing ammonium bromocamphorsulphonate with zinc dust and ammonia (Kipping and Pope, Trans., 1895, 67, 358); after precipitating the zinc with hydrogen sulphide, the solution was boiled with baryta until free from ammonia, and then the barium exactly precipitated with dilute sulphuric acid; the filtrate, on evaporation, gave a syrup which was freed from hydrogen bromide by repeatedly taking up with water, and finally by treating with precipitated silver oxide.

The salt, prepared by neutralising the aqueous solution of the acid with externally compensated hydrindamine and then evaporating to a moderate bulk, crystallised in large, fairly well-defined plates or prisms,

* If the constitution of bromocamphorsulphonic acid be really represented by the above formula, as there are good reasons for supposing it to be, the formation of optically different forms of this and of the corresponding α-chloro- and halogen-free acids by the displacement of hydrogen from different methyl groups would seem to be not improbable, but hitherto no such isomerides have been discovered.

and on further concentration the mother liquors gave successive deposits, apparently all of the same kind. On repeatedly recrystallising the several fractions from water or dilute alcohol, they all seemed to be homogeneous, and neither the appearance nor the melting point of the new deposits showed any indication of the presence of isomerides; when, however, after some 15 to 20 operations, the specific rotation of the first or most sparingly soluble, and that of the last or most readily soluble, fraction were determined, a slight difference was sometimes noted, and on further recrystallisation of the most sparingly soluble fraction until it had been reduced to about 2 per cent. of the original salt, this difference became well-marked, as shown by the following determinations:

Sparingly soluble fraction: 0·5288 gram of the air-dried salt was dissolved in 99·8 per cent. ethyl alcohol, the solution diluted to 25 c.c., and examined in a 200 mm. tube: $\alpha_D = +1°38'$, $[\alpha]_D = +38·5°$.

Readily soluble fraction: 0·5245 gram of the air-dried salt under the same conditions gave $\alpha_D = +2°3'$, $[\alpha]_D = +48·8°$.

The specific rotations were also different in aqueous solution; dissolving 0·5 gram in each case and diluting to 25 c.c., the air-dried preparations gave the following results in a 200 mm. tube:

Sparingly soluble fraction: $\alpha_D = +1°13'$, $[\alpha]_D = +30°$.
Readily soluble fraction: $\alpha_D = +1°37'$, $[\alpha]_D = +40·2°$.

As these two preparations appeared to represent isomeric partially racemic salts analogous to the hydrindamine bromocamphorsulphonates (*loc. cit.*), considerable quantities of the crude material were prepared and fractionated, but, as there was no indication of any separation having occurred, many of the most sparingly soluble portions were found at first to have a specific rotation practically identical with that of the readily soluble fractions; on further crystallisation, however, it always seemed possible to obtain a sample having a specific rotation of about $+30°$ in aqueous solution, that of the main product being from $+40°$ to $+42°$.

The apparently constant values of the specific rotations of the two preparations seemed to stamp them as definite, but different, compounds, notwithstanding their great similiarity in other properties; when crystallised from various solvents and then examined under the microscope, the two preparations showed no noteworthy difference, except that the more readily soluble substance usually formed the more well-defined crystals; the melting points of the two preparations were also very close together, the more sparingly soluble portion melting at about 201—202°, the other at about 197—198°, but in both cases the rate of heating and the size of the crystals affected the result, so that

too much weight could not be attached to the observed difference in behaviour. Analyses showed that the salts were isomeric and contained practically the same amount of water of crystallisation.

Sparingly soluble salt:

0·5006 air-dried salt lost 0·0216 H_2O at 100°. $H_2O = 4·3$.
0·2309 anhydrous salt gave 0·1500 $BaSO_4$. $S = 8·9$.

Readily soluble salt:

0·5069 lost 0·0249 H_2O at 100°. $H_2O = 4·8$.
0·2604 anhydrous salt gave 0·1653 $BaSO_4$. $S = 8·7$.
$C_9H_{11}N,C_{10}H_{15}O·SO_3H,1\frac{1}{4}H_2O$ requires $H_2O = 4·7$ per cent.
$C_9H_{11}N,C_{10}H_{15}O·SO_3H$ „ $S = 8·7$ per cent.

In order to obtain further evidence in favour of the view that these preparations were both partially racemic salts, it was necessary to compare their molecular rotations with that of camphor-π-sulphonic acid; the ammonium salt of this acid was therefore prepared and anhydrous samples used in the following determinations:

0·5 gram dissolved in water and the solution diluted to 25 c.c. gave in a 200 mm. tube $\alpha_D = +2°39·5'$, $[\alpha]_D = +66·5°$, and in a second experiment, $\alpha_D = +2°41'$, $[\alpha]_D = +67°$.

The molecular rotation of the acid, calculated from these results, is $[M]_D = +166°$.

Taking the values $[\alpha]_D = +30°$, 31°, 30·4°, 30·5°, which had been obtained with various air-dried samples, for the specific rotation of the more sparingly soluble salt, the molecular rotation was $[M]_D = +111°$, that of the isomeride, which gave $[\alpha]_D = +40°$, 42·7°, 42·5°, being about 155°; the values for the anhydrous salts would be therefore +117° and 163° respectively.

So large a difference between the calculated and observed values, in the case of the more sparingly soluble salt, aroused suspicion as to its supposed partially racemic character, and the following experiment was therefore made:

0·5 gram of air-dried salt was dissolved in water, and the solution, after diluting to 25 c.c., was examined in a 200 mm. tube; the mean of many concordant readings gave $\alpha_D = +1°9'$.

The whole of this solution was then carefully washed into a flask, and the theoretical quantity of $N/10$ sodium hydroxide necessary to liberate the base was added; after boiling until all the hydrindamine had been expelled, the solution was again made up to 25 c.c. and examined in a 200 mm. tube.

The average reading was now +1°10′, so that the specific rotation

had undergone no change, and the molecular rotation calculated from this result was about $+107°$, or, allowing for the water of crystallisation, about $+112°$.

This experiment proved, therefore, that the low molecular rotation of the sparingly soluble salt was in no way connected with the presence of hydrindamine, but depended entirely on the acid, and as the analysis of the salt showed it to be a pure hydrindamine camphorsulphonate, the only conclusion to be drawn was that the sparingly soluble salt contained an acid isomeric with, but optically different from, *d*-camphorsulphonic acid.

The practically constant values obtained for the specific rotation of different preparations of the more sparingly soluble salt seemed to indicate a homogeneous substance, but on repeatedly recrystallising a sample of about 3 grams ($[\alpha]_D = +30°$) from water and dilute alcohol, the specific rotation in aqueous solution fell from $+30°$ to $+16°$, then to $+10{\cdot}5°$, and finally to $+8{\cdot}8°$, after which, partly owing to lack of material and partly because no further change seemed to occur, further fractional crystallisation was not attempted.

The results of the last experiments still left open the question as to the nature of the isomeric acid, although they seemed to indicate the presence of an optically inactive salt; that the isomeride is enantiomorphously related to the *d*-acid was, however, proved as follows.

A sample of salt having a specific rotation about $[\alpha]_D = +15°$ was triturated with phosphorus pentachloride, and the sulphonic chloride, isolated in the usual manner, was then examined; on fractionally extracting it with boiling light petroleum, the first extracts gave deposits of fern-like masses, which in appearance were indistinguishable from the crystals of externally compensated or pseudoracemic camphorsulphonic chloride (Kipping and Pope, Trans., 1893, 63, 560); the melting point of these deposits, as well as their behaviour on re-melting, was also that of the optically inactive chloride. Further, on crystallising these deposits from ethyl acetate, small, transparent, four-sided plates, exactly like those of the pseudoracemic compound (*loc. cit.*, p. 562), were observed.

There can be little doubt, therefore, that the sparingly soluble fractions of the hydrindamine camphorsulphonate contain a lævorotatory acid, which is enantiomorphously related to the *d*-acid, of which probably at least 95 per cent. of the crude acid consists.

Nature of the Salts.

The fact that the *d-l*-hydrindamine *d-l*-camphorsulphonate accumulates in the more sparingly soluble portions, whilst a practically pure, partially externally compensated salt is deposited from the

final mother liquors, on crystallising the mixture of the two, seems to show that the *d*- and *l*-acids, when combined with the *d*- and *l*-bases, form a racemic compound.

The case, however, does not appear to be quite so simple as those which have been dealt with theoretically by Bakhuis-Roozeboom (*Zeit. physikal. Chem.*, 1899, **28**, 494), who has so ably discussed the principles of the methods by which a racemic compound can be distinguished from a non-racemic mixture.

On neutralising the mixture of the *d*- and *l*-acids with the externally compensated base, the following four salts will be produced:

$$d\text{A}d\text{B},\ d\text{A}l\text{B},\ l\text{A}d\text{B},\ l\text{A}l\text{B},$$

of which the first two will be present in large excess; the salt which is finally obtained in the most sparingly soluble fraction, $[\alpha]_D = +9°$, is therefore a mixture of about four parts of $l\text{A}d\text{B}$, $d\text{A}l\text{B}$, or of $l\text{A}l\text{B}$, $d\text{A}d\text{B}$, to one of $d\text{A}d\text{B}$, $d\text{A}l\text{B}$, whilst from the final mother liquors, the salt, $d\text{A}d\text{B}$, $d\text{A}l\text{B}$, is deposited in a practically pure condition.

Now, since $d\text{A}d\text{B}$ and $d\text{A}l\text{B}$ are equally soluble, because the base contained in the last fractions of the salt is optically inactive, and the solubility of $l\text{A}d\text{B}$ must be the same as that of $d\text{A}l\text{B}$, it would seem that $d\text{A}l\text{B}$, of which there is a much larger quantity than of $l\text{A}d\text{B}$, should crystallise out before the latter, unless they form together a more sparingly soluble racemic salt which causes the separation of $l\text{A}d\text{B}$ with $d\text{A}l\text{B}$.

That the solubility of the salt-pair, $l\text{A}d\text{B}$, $d\text{A}l\text{B}$ (or $l\text{A}l\text{B}$, $d\text{A}d\text{B}$), is very different from that of the partially externally compensated salt, $d\text{A}d\text{B}$, $d\text{A}l\text{B}$, is shown by the following determinations.

A sparingly soluble fraction, $[\alpha]_D = +29°$, was shaken with water until the solution was saturated at 14°; the solubility was found to be 3·5 parts of anhydrous salt in 100 parts by weight of water. A readily soluble fraction, $[\alpha]_D = +42°$, treated in a similar manner, dissolved to the extent of 8·7 parts of anhydrous salt in 100 of the solvent.

The specific rotations of the anhydrous samples, obtained by evaporating to dryness the two solutions and then heating at 100° until constant, were determined in aqueous solution, with the following results:

Sparingly soluble: 0·1773 gram : volume 25 c.c. 200 mm. tube. $\alpha_D = +37'$; $[\alpha]_D = +43·4°$.

Readily soluble: 0·5107 gram under the same conditions, $\alpha_D = +1°52'$; $[\alpha]_D = +45·8°$.

The value for the readily soluble salt gives a molecular rotation

of $[M]_D = +167°$, which is very close to that of ammonim camphor-π-sulphonate, showing that the salt contains equal quantities of *d*A*d*B and *d*A*l*B. The results obtained with the mixture of the salts of the *d*- and *l*-acids seem to indicate the existence of a racemic compound; as already stated, the melting point of the mixture is about 5° higher than that of the partially externally compensated salt, but here again the evidence is inconclusive.

The partially externally compensated salt separates from cold water in large, transparent, rhomboidal prisms, which become opaque when heated alone or in contact with the mother liquor; it is readily soluble in boiling water and cold alcohol, but only very sparingly so in boiling ethyl acetate, and practically insoluble in ether.

Having defrayed part of the cost of the material used in this work out of a Goverment grant, it is the author's pleasant duty to express his gratitude to the Government Grant Committee of the Royal Society for the help thus extended.

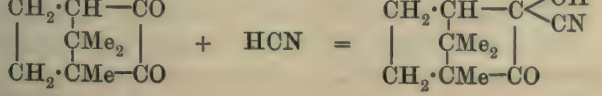
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NOTTINGHAM.

XXXIX.—*aa-Hydroxycamphorcarboxylic Acid.*

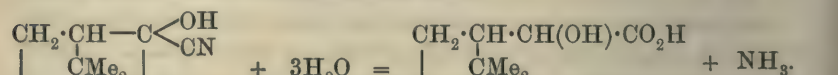
By ARTHUR LAPWORTH and EDWIN M. CHAPMAN.

IT has recently been shown by one of us (Trans., 1900, 77, 1061) that when *a*-chloro- or *a*-bromo-cyanocamphor is heated with potash, it does not undergo a simple hydrolysis as does cyanocamphor itself, but it is, in part, reduced, probably in the first instance to cyanocamphor, so that *a*-substituted homocamphoric acids cannot be obtained by this method. It appeared almost certain, however, that *a*-hydroxycyanocamphor or *a*-hydroxycamphorcarboxylic acid would not be prone to undergo such a preliminary reduction, and might therefore readily yield *a*-hydroxyhomocamphoric acid or its lactone, from which the corresponding halogenised acid could be prepared.

Attempts to replace the halogen atom of bromo- or chloro-cyanocamphor by hydroxyl were without result, and an entirely different mode of preparing the hydroxy-compound was tried; namely, by the addition of hydrogen cyanide to camphorquinone:



The new compound would not, of course, yield hydroxyhomocamphoric acid on alkaline hydrolysis, as α-hydroxynitriles at once lose hydrogen cyanide under these conditions, but, by hydrolysis in acid solution, it was hoped that the carboxylic acid could be prepared and that this, on treatment with strong alkali, would break up like other β-ketonic acids, including camphorcarboxylic acid itself, affording the desired derivative of homocamphoric acid:



Whilst some of these anticipations have been realised, much difficulty was experienced in obtaining good yields of the products, owing mostly to the resistance offered by the nitrile and the amide to hydrolysis, and as the desired homocamphoric acid derivatives had been obtained meanwhile by another method (Trans., 1900, 77, 1066), the investigation was discontinued. Some of the observations which were made, however, are thought worthy of record.

Camphorquinone readily unites with nascent hydrogen cyanide under the proper conditions, affording a camphoraceous substance which has all the properties of an α-hydroxynitrile, and regenerates the quinone when heated, or when treated with alkalis. The nitrile is very stable towards acids, however, and is only very slowly hydrolysed, even with hot hydrochloric acid, or 60 per cent. sulphuric acid; when mixed with cold fuming sulphuric acid, however, it dissolves without appreciable charring, and on pouring this solution into water, a bulky precipitate is obtained, from which the amide of hydroxycamphorcarboxylic acid may be isolated. Judging from the fact that the whole of the substance precipitated has the same general properties as the purified amide, and yet yields only a certain proportion of what can undoubtedly be regarded as an individual substance, it would appear to be a mixture of amides, probably stereoisomeric, but we found it impossible to isolate more than one modification in spite of careful fractionation with various solvents. The amide thus produced is not less stable towards acids than is the original nitrile, and only by prolonged heating with fuming hydrobromic acid could any large proportion of it be converted into the carboxylic acid; the use of nitrous acid, which has so frequently been found of value in the case of other stable amides, was here practically useless, as the products obtained could only be crystallised with difficulty.

α-Hydroxycamphorcarboxylic acid, obtained from the purified amide, has all the characters of an α-hydroxy-acid. It is readily oxidised by acetic acid and lead peroxide, affording camphorquinone, and on distillation loses carbon dioxide, yielding hydroxycamphor, identi-

cal, as was to be expected, with the substance obtained by Manasse on reducing camphorquinone with zinc dust and acetic acid (*Ber.*, 1897, **30**, 659). It yields an acetyl derivative when treated with acetyl chloride, and is decomposed on prolonged boiling with alkali, probably being hydrolysed with formation of *a*-hydroxyhomocamphoric acid, but owing to the small quantity of acid which we were able to obtain, this point was not decided, and experiments with the impure homocamphanic acid prepared from *a*-bromohomocamphoric acid showed that its isolation in a crystalline state is frequently a matter of considerable difficulty, even when fairly large quantities are available.

A question which naturally suggests itself in relation to the above processes concerns the position which is attacked by the hydrogen cyanide, and it might be thought that no positive statement could be made as to which of the two carbonyl groups in camphorquinone would be the more reactive. This, however, is not the case, as there can no longer be any doubt that a carbonyl group of a ketone or an acid is more or less reactive according as it is attached to a primary, secondary, or tertiary carbon atom. The well-known case of the difficulty experienced in esterifying a carboxyl group in the complex, $\begin{matrix}C\\C\!-\!\end{matrix}\!\!>\!C\cdot CO_2H$, is doubtless only a special instance of the applicability of this principle, and it appears that the unsaturated group in the complex, $\begin{matrix}C\\C\!-\!\end{matrix}\!\!>\!C\cdot X\!:\!Y$, has an exceptionally feeble power of forming additive compounds, a fact exemplified by camphor itself, which shows no inclination whatever to combine with hydrogen cyanide.

Taking the case, then, of camphorquinone, it is certain that one carbonyl group, namely, that representing the original carbonyl group of camphor, is attached to a tertiary carbon atom, whilst the other, representing the $\cdot CH_2\cdot$ group of camphor, is affixed to a $:CH$ group, so that it should be correspondingly reactive. These considerations and the observed inability of camphor itself to combine with hydrogen cyanide (Alvisi, *Gazz.*, 1893, **22**, i, 265), make it practically certain that the hydroxynitrile obtained from camphorquinone is *aa'*-hydroxycyanocamphor and not the isomeride.

As more direct evidence of the truth of the foregoing conclusion may be cited the fact that camphorquinone phenylhydrazone is identical with the substance obtained by the action of diazobenzene on *a*-camphorcarboxylic acid (*Annalen*, 1892, **274**, 87 ; 1894, **281**, 347), showing that the carbonyl group of the quinone which is most liable to attack is not the one which is present in camphor itself.

Experimental.

Preparation of Camphorquinone.—This substance was first obtained from *iso*nitrosocamphor by the use of nitrous acid, and in smaller quantities by boiling the substance with sodium bisulphite solution (Claisen and Manasse, *Annalen*, 1892, **274**, 84). The yield by either method as described by these authors is poor, and, in the case where nitrous acid is used, the quinone obtained, although apparently homogeneous, is always contaminated with large quantities of camphoric anhydride, from which it is a matter of difficulty to free it. These facts have already been noted by Manasse (*Ber.*, 1897, **30**, 662) who in the same place states that, by a modification of the bisulphite method which is not described, he was able to obtain the pure substance in quantities occasionally as great as 80 per cent. of the theoretical.

It occurred to us that a good yield of the quinone might be obtained by using *iso*nitrosocamphor in solution, instead of in the solid state, and producing sodium hydrogen sulphite in the solution, and although we have not succeeded in obtaining quite so good a yield as that mentioned by Manasse, the following method appears to be more satisfactory than any hitherto described.

*iso*Nitrosocamphor (25 grams) is dissolved in glacial acetic acid (45 c.c.) and to the solution is added slowly finely powdered hydrated sodium sulphite (100 grams), the mixture being shaken vigorously and warmed over a naked flame during the addition; the whole is boiled for an hour on a sand-bath under a reflux condenser, hydrochloric acid (100 c.c.) is then slowly added to the boiling solution, and the heating continued for half an hour, when the liquid is diluted with water, cooled, and filtered, the yellow precipitate of camphorquinone being submitted to distillation in a current of steam.

Camphorquinone p-*Bromophenylhydrazone*, $C_{10}H_{14}O{:}N{\cdot}NH{\cdot}C_6H_4Br$, is formed when very dilute solutions of *p*-bromophenylhydrazine acetate and camphorquinone are mixed, and is precipitated as a yellow, granular powder. It may be crystallised from a large bulk of glacial acetic acid and forms small, bright yellow, transparent, rhombohedral crystals; it melts at 215—216° without appreciable decomposition, but does not afterwards solidify readily. On analysis:

0·3314 gave 0·1824 AgBr. Br = 23·4.

$C_{16}H_{19}ON_2Br$ requires Br = 23·8 per cent.

It is sparingly soluble in ethyl or methyl alcohol, acetone, ethyl acetate, or formic or acetic acid, very sparingly so in chloroform or benzene, and nearly insoluble in light petroleum. The slight solubility

of this substance renders it an easy matter to test for camphorquinone, even when present in very small quantity.

The hydrazone dissolves readily in cold strong sulphuric acid, forming a bright yellow solution which, on addition of a little nitric acid, becomes successively brilliant green, pink, and finally colourless.

Betti (*Ber.*, 1899, **32**, 1995) has shown that camphorquinone phenylhydrazone exists in two desmotropic modifications, the form usually obtained being *enolic*, and yielding in benzene solution a red coloration with ethereal ferric chloride, whilst the *ketonic* form is isolated by treating saturated solutions of the *enolic* form with a little piperidine, when crystals of the second modification are deposited. We have only been able to obtain the *p*-bromophenylhydrazone in one form, and that appears to be the ketonic modification, as it yields no coloration whatever with ferric chloride.

Camphorquinonesemicarbazone, $C_{10}H_{14}O{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$.—This substance is obtained by adding to camphorquinone dissolved in a little alcohol the calculated quantity of semicarbazide hydrochloride and sodium acetate dissolved in water, and warming on the water-bath for a short time; the colour of the quinone gradually disappears and the semicarbazone is isolated by driving off the alcohol on the water-bath, adding water to the residue, and crystallising the undissolved portion from dilute methyl alcohol.

The substance thus obtained is practically colourless, and separates from methyl alcohol in elongated, apparently orthorhombic plates, having straight extinction, the direction of greatest length being coincident with that of least elasticity. When heated, it turns yellow at 210°, and melts and decomposes at 228—229°. On analysis:

0·1940 gave 0·4168 CO_2 and 0·1346 H_2O. C = 58·6; H = 7·7.
$C_{11}H_{17}ON_3$ requires C = 59·1; H = 7·6 per cent.

It is somewhat striking that this substance should be so nearly colourless, when it is considered that the analogous hydrazones and the quinone from which it is derived are all strongly coloured, and it is at first thought probable that some structural change had occurred. It was therefore hydrolysed by warming with hydrochloric acid, but a yellow colour at once appeared, and, after half an hour, addition of excess of sodium acetate and *p*-bromophenylhydrazine acetate produced a precipitate of the characteristic camphorquinone *p*-bromophenylhydrazone.

a-Hydroxycyanocamphor, $C_8H_{14}\begin{cases}C(OH){\cdot}CN\\ |\\ CO\end{cases}$.

Camphorquinone (5 grams) mixed with finely powdered potassium cyanide (15 grams) is placed in a flask and covered with 25 c.c. of

pure dry ether, and cooled with a mixture of ice and salt. To the liquid, glacial acetic acid is then added from a tap funnel in small quantities at a time, when in the course of a few minutes the colour of the quinone disappears. An equal bulk of water is then added, the whole well shaken, and the ether separated and allowed to evaporate spontaneously. A yellowish oil remains, which can be converted into a solid material by trituration with moderately strong acids, as these appear to remove in some way the impurities which prevent crystallisation.

The hydroxynitrile may be partially purified from light petroleum, but, in spite of frequently repeated attempts, no large quantity of it has been obtained in a pure state, and it appears to be a mixture of nitriles, probably stereoisomerides. By repeated crystallisation, a small quantity of a substance may be obtained in the form of well-defined, six-sided orthorhombic plates, in which the directions of greatest length and elasticity are at right angles. When heated, these crystals turn yellow, and melt at 197—198°, which is approximately the melting point of camphorquinone, to which, at about this temperature, the substance probably reverts.

The nitrile has all the general properties of α-hydroxynitriles. It is decomposed at once by alkalis, hydrocyanic acid and camphorquinone being regenerated, but is very stable towards acids, and may be heated at 100° with strong hydrochloric acid for several days without suffering complete conversion into the hydroxy-acid. It dissolves in common sulphuric acid, and is precipitated practically unchanged on dilution; with fuming sulphuric acid, however, it is converted into the hydroxyamide.

Hydroxycamphorcarboxylic amide, $C_8H_{14}<\begin{matrix}C(OH)\cdot CO\cdot NH_2\\ CO\end{matrix}$.

Hydroxycyanocamphor is dissolved in an equal weight of ordinary sulphuric acid, and the solution poured into about twice its bulk of fuming sulphuric acid, containing about 20 per cent. of anhydride; the whole is then poured into a large bulk of water, and the resulting bulky white precipitate collected on a filter. This substance is the amide, corresponding with the hydroxynitrile, but is certainly not a uniform substance; on crystallisation from acetone, however, it readily yields about one-third its weight of a well-crystallised substance, of which a specimen was analysed:

0·1890 gave 0·4352 CO_2 and 0·1389 H_2O. C = 62·8; H = 8·1.

$C_{11}H_{17}O_3N$ requires C = 62·6; H = 8·1 per cent.

The amide is insoluble in light petroleum, very sparingly soluble in hot benzene or chloroform, and sparingly so in hot acetone or cold

alcohol, but dissolves moderately readily in hot alcohol. It is best crystallised from hot acetone, from which it separates on cooling in hard, lustrous, transparent prisms, which, when heated, sublime slowly and finally melt, somewhat indefinitely, at 235—240°.

The crystals are well-formed orthorhombic prisms, which show the forms {100}, {010}, and {011}, the angle 101—10$\bar{1}$ being about 124°. They are extended in the direction of the *a*-axis, and usually flattened in that of the *b*-axis. The acute bisectrix is the *a*-, the obtuse being the *b*-axis. The elasticity in the direction of the *a*-axis exceeds that along the *c*-axis, so that the double refraction is negative. It is difficult to obtain a specimen melted between glass slips, owing to the rapidity with which the substance sublimes at about its melting point; but it was found to solidify in very well-formed needles or long, flat plates of the same type as the crystals from acetone. It distils with very little decomposition when heated, and is very stable towards hydrolytic agents in general. Attempts to convert it into the acid by means of sodium nitrite were unsuccessful, as the products failed to crystallise.

a-Hydroxycamphorcarboxylic acid, $C_8H_{14}<\begin{matrix}C(OH)\cdot CO_2H\\ CO\end{matrix}$.

In order to prepare this acid, the nitrile is boiled with hydrochloric acid for several days, and, without waiting for complete conversion, the liquid is evaporated to dryness and extracted with a solution of sodium carbonate. The solution of the sodium salt is evaporated, acidified, and extracted with ether; on evaporation, the hydroxy-acid is left as a white mass of interlaced, glistening needles.

It may also be prepared from the purified amide by heating this with strong hydrobromic acid. The crude amide appears to be useless for the purpose, as it yields an indefinitely crystalline mass which is difficult to resolve into the pure constituents. It may be crystallised from a mixture of ethyl acetate and petroleum. A specimen was dried at 100° and analysed:

0·1969 gave 0·4508 CO_2 and 0·1336 H_2O. C = 62·4; H = 7·5.

$C_{11}H_{16}O_4$ requires C = 62·2; H = 7·5 per cent.

Hydroxycamphorcarboxylic acid dissolves sparingly in water, readily in ethyl acetate, acetone, methyl or ethyl alcohol, or acetic acid, but is nearly insoluble in chloroform, benzene, or petroleum. It crystallises from a mixture of ethyl acetate and petroleum in brilliant, colourless needles or prisms, which melt and decompose at 207—208°.

The crystals are six-sided, orthorhombic plates, having straight extinction, and the directions of greatest length and elasticity are coincident. It is almost impossible to obtain a specimen melted

between glass slips, owing to the rapidity with which it decomposes; a few isolated needles resembling the small crystals from solution are, however, occasionally observed.

It is a monobasic acid; 0·1625 required 7·45 c.c. $N/10$ soda for neutralisation, whence the equivalent of the acid is 218, the calculated number being 212.

A dilute solution of the sodium salt gave no precipitate with salts of barium, copper, manganese, cobalt, nickel, chromium, bismuth, or mercury, but with lead acetate or calcium chloride a precipitate is produced on boiling; with ferric chloride, a red solution is obtained which affords a precipitate when boiled.

Hydroxycamphorcarboxylic acid, although containing a carbonyl group, does not afford precipitates when boiled with solutions of hydrazine or semicarbazide acetate, and does not react with hydroxylamine. The retarding effect of the α-substituents on the reactivity of the carbonyl group is thus clearly brought out.

Attempts were made to prove the constitution of the acid by replacing its hydroxyl group with chlorine, which should have afforded ordinary chlorocyanocamphor; on treating the substance with phosphorus penta- or tri-chloride, hydrogen chloride was evolved, but action appeared to cease with the formation of the acid chloride, and on treating the product with anhydrous formic acid, all that could be isolated in a crystalline form was the unaltered hydroxy-acid. When boiled for a long time with strong potassium hydroxide solution, the acid was decomposed, but on acidifying the product and extracting with ether, only oily products could be isolated.

In accordance with the fact that it is an α-hydroxy-acid, it is readily oxidised, with loss of carbon dioxide. A small quantity was dissolved in dilute acetic acid through which a current of steam was passed, and was treated with successive small quantities of lead peroxide. Carbon dioxide was rapidly evolved and the distillate assumed a yellow colour, due to camphorquinone, as was shown by adding a solution of p-bromophenylhydrazine acetate. The small quantity of a yellow precipitate obtained was collected and crystallised from glacial acetic acid, when small brilliant crystals of camphorquinone p-bromophenylhydrazone melting at 216° were deposited.

Action of Heat on Hydroxycamphorcarboxylic acid.—When the acid is heated at its melting point, it rapidly loses carbon dioxide, and if the residue is then distilled in a current of steam, a solid substance, having an unpleasant, camphoraceous odour, passes over. The distillate was saturated with ammonium sulphate and the insoluble matter collected, dried, and crystallised from a mixture of benzene and light petroleum, when it formed a mass of white needles melting at 205—206°. On analysis:

0·2089 gave 0·5460 CO_2 and 0·1850 H_2O. C = 71·2 ; H = 9·8.
$C_{10}H_{16}O_2$ requires C = 71·5 ; H = 9·5 per cent.

When heated beneath a cover-glass on a microscope slide, the substance set to a transparent mass, with few indications of a crystalline structure, and was completely isotropic. It sublimed with great readiness, dissolved sparingly in water, and was precipitated from the solution on addition of metallic salts. Its properties were, in fact, identical with those of the α-hydroxycamphor obtained by Manasse on reducing camphorquinone with zinc dust and acetic acid (*Ber.*, 1897, 30, 659).

α-Acetoxycamphorcarboxylic acid, $C_8H_{14}<\begin{matrix}C(OAc)\cdot CO_2H\\ CO\end{matrix}$.

On treating hydroxycamphorcarboxylic acid with acetyl chloride, in which it is insoluble, hydrogen chloride is slowly evolved, even in the cold, and the acid dissolves. On filtering the solution and evaporating to dryness, a colourless, oily mass remained, which, on exposure over caustic potash in a vacuum, showed no tendency to crystallise. It was therefore extracted repeatedly with small quantities of light petroleum and the fractions allowed to evaporate spontaneously. From several of these fractions, fine needles were deposited, and were collected and recrystallised from a mixture of ethyl acetate and light petroleum. A specimen was analysed :

0·1689 gave 0·3804 CO_2 and 0·1085 H_2O. C = 61·3 ; H = 7·1.
$C_{13}H_{18}O_5$ requires C = 61·4 ; H = 7·1 per cent.

The acetyl compound is practicably insoluble in cold water, but dissolves at once in dilute sodium carbonate solution, carbon dioxide being liberated. It is sparingly soluble in cold, light petroleum, and only moderately so in cold benzene; it dissolves very readily in chloroform, alcohol, acetone, ethyl acetate, or acetic acid, and crystallises in glistening, felted needles melting at 85—86°.

When melted between glass slips, it solidifies very slowly and incompletely at the ordinary temperature, and not much more rapidly at a temperature approaching its melting point. The solidified portion consists of curious, irregularly-shaped, flattened needles of the same crystallographic type as those deposited from solution ; the extinction is straight, and the directions of greatest length and optical elasticity are at right angles to one another.

When heated at temperatures above 150°, the compound loses carbon dioxide more or less rapidly, being doubtless converted into the acetyl derivative of hydroxycamphor, but, as was found by Manasse, the substance showed no tendency to crystallise.

When the acid is warmed with 75 per cent. sulphuric acid, and the

resulting solution heated in a current of steam, the distillate gives all the characteristic tests for acetic acid.

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XL.—*The Bacterial Decomposition of Formic Acid into Carbon Dioxide and Hydrogen.*

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THE action of the lower organisms on chemical substances has been frequently investigated, in order, if possible, to discover a case of bacterial decomposition of a chemically simple nature, which might serve to elucidate the action of bacteria on organic compounds in general; that this end has so rarely been obtained we are inclined to attribute to the fact that comparatively complex substances, such as the sugars, have hitherto formed the main subjects of investigation. We therefore instituted a search for compounds of very simple molecular composition which should be attacked by the commoner organisms, and have succeeded in proving definitely that various bacteria in pure culture decompose formic acid directly into equal volumes of carbon dioxide and hydrogen.

Hoppe-Seyler observed (*Zeit. physiol. Chem.*, 1887, 11, 566) that on bacterially infecting a calcium formate solution with river mud, equal volumes of carbon dioxide and hydrogen were evolved. At a later date, P. F. Frankland and his pupils independently concluded (Trans., 1892, 61, 270, 432, 737) that a similar decomposition occurs as one stage during the action of the *Bacillus ethaceticus* and Friedländer's *Pneumobacillus* on mannitol.

Since the *Bacillus coli communis* and others of the bacteria with which we have been working are frequently found in river mud, our present results are in a measure confirmatory of those of Hoppe-Seyler.

Kitasato has observed that the addition of sodium formate to media containing *d*-glucose materially assists the growth of certain bacteria under anaerobic conditions; he, however, gives no details as to the nature of the gaseous products. We have confirmed his results

and made the further observation that the gases produced from media containing *d*-glucose and sodium formate differ both in volume and composition from those evolved from a medium differing only from the former in that it contains no sodium formate.

The gases produced by the action of the *Bacillus coli communis* upon *d*-glucose in a solution of meat extractives containing peptone have been examined by Th. Smith, Chantemesse, Lehmann and Neumann, and others, who agree that the constituents are carbon dioxide, hydrogen, and nitrogen, but differ widely as to the value of the ratio $CO_2 : H_2$. The proportion of carbon dioxide in the mixture is variously stated to be from 25 to 50 per cent. by volume.

On analysing the gases produced from *d*-glucose, using the method of collection and analysis previously described (Pakes and Jollyman, this vol., p. 322), we find that the amount of gas evolved per 100 c.c. of medium depends upon the particular organism dealt with. The medium ("M") used for the following experiments was made by extracting lean meat with ordinary tap water, coagulating the proteid by heat, and filtering; 1 per cent. of Witte's peptone and 0·5 per cent. of sodium chloride are subsequently added. After addition of the other constituents mentioned in each series of experiments, the whole is heated in the steamer and neutralised with *N* caustic soda.

Series I. "M" with 2 per cent. of *d*-glucose.

Organism.	Total gas evolved from 100 c.c. of medium.	Percentage volume of carbon dioxide.
B. coli communis	32·8 c.c.	31·5 per cent.
B. enteritidis of Gärtner	68·6	35·4 ,,
Pneumobacillus of Friedländer	10·9	22·2 ,,
B. maligni œdematis	36·4	40·0 ,,

The medium "M," alone, yields but a small quantity of gas when planted with these organisms; thus the *B. coli communis* gave 5·7 c.c. of gas per 100 c.c. of medium and this contained 17·8 per cent. of carbon dioxide, 58·2 per cent. of hydrogen, and 23·9 per cent. of nitrogen.

The addition of sodium formate to the medium "M" containing 2 per cent. of *d*-glucose gave the following results:

Series II. "M" with *d*-glucose and sodium formate.

(i) October 15th.—Four hundred and ninety c.c. of the medium "M" containing 2 per cent. of *d*-glucose and 0·5 per cent. of sodium formate were inoculated with the *B. coli communis*, attached to the gas receiver of the apparatus already described (*loc. cit.*) and incubated under strictly anaërobic conditions. The gas evolved was drawn off day by day and analysed, with the following results:

Oct.	16th.	Gas produced	390	c.c. containing	34·2	per cent. CO_2.
„	17th.	„	298	„	—	„
„	18th.	„	399	„	48·8	„
„	19th.	„	146	„	56·0	„
„	20th.	„	169·6	„	57·2	„

e residual gas was found to be hydrogen with a daily decreasing quantity of nitrogen. After the termination of the experiment the medium was very acid to litmus and therefore all the carbon dioxide had been evolved as gas.

(ii) November 5th.—A flask containing 425 c.c. of the same medium containing *d*-glucose and 0·4 per cent. of sodium formate was inoculated with the *B. coli communis* and joined to the gas receiver.

Nov.	6th.	Gas produced	473	c.c. containing	36·4	per cent. CO_2.
„	7th.	„	428	„	44·0	„
„	8th.	„	292	„	54·0	„
„	9th.	„	226·8	„	57·3	„
„	10th.	„	97·9	„	56·4	„
„	12th.	„	92·0	„	58·0	„
„	21st.	„	65·0	„	52·3	„

As before, the residual gas was hydrogen and a small amount of nitrogen. At the end of the experiment, the medium was very acid to litmus.

Similar results were obtained when the same medium was inoculated with the *B. enteritidis* of Gärtner, the *Pneumobacillus* of Friedländer, and the *Bacillus* of malignant œdema.

The increasing percentages of carbon dioxide in the evolved gases led to the conclusion that a certain amount of alkali was produced—probably from the formate—which neutralised the acids produced by the bacteria from the sugar. This neutralisation allowed the bacteria to attack more of the sugar and so to produce more gas. Similar results can be obtained by placing about 1 per cent. of calcium carbonate in the medium.

In order to determine whether the alkali was derived from the formate, we omitted the *d*-glucose from the medium and substituted 1 per cent. of sodium formate. This was placed in test-tubes which were severally inoculated with the above-named bacteria and incubated. At the end of 24 hours, there was a definite froth upon the surface, and at the end of 48 hours the medium was distinctly alkaline.

Many experiments have been performed with this medium, but the following will serve as an example.

Series III. "M" with sodium formate.

October 22nd.—A flask containing 490 c.c. of meat extract in water

with 1 per cent. of sodium formate, and neutralised, was inoculated with the *B. enteritidis* of Gärtner and connected to the gas receiver.

Oct. 23rd.	Gas produced	66·8 c.c.	containing	12·0	per cent. CO_2.
„ 24th.	„	104·4	„	19·9	„
„ „	„	97·8	„	20·8	„
„ 25th.	„	121·0	„	21·3	„
„ 26th.	„	101·0	„	21·1	„
„ 27th.	„	44·4	„	21·8	„
„ 28th.	„	27·0	„	20·0	„
Total (exclusive of 1st)		495·6	Average	20·7	„

The fact that the percentage of carbon dioxide remained so constant throughout the experiment suggested that the formate was decomposed in one stage, no secondary reactions occurring, and although it was impossible to determine the alkalinity of the medium during the progress of the experiment, we determined subsequently that it does increase day by day until no further gas is evolved.

In order to determine the amount of carbon dioxide retained in the medium as bicarbonate, the flask was first carefully disconnected from the receiver. A second receiver, full of mercury, was then connected to a small flask fitted with a rubber cork carrying a piece of glass tubing bent at right angles and a thistle tube descending to the bottom of the flask. By means of a pipette, 20 c.c. of the medium were transferred to the small flask, the cork replaced, and an excess of pure sulphuric acid was run into the fluid through the funnel. The contents of the flask were then well boiled and all the air and gas driven over into the receiver; while the contents of the flask were still boiling, the tap of the receiver was turned and the flask quickly disconnected. The gas in the receiver was allowed to cool and the carbon dioxide present determined. The determination was several times repeated and the average result found to be that each 20 c.c. of medium retained 14·3 c.c. of carbon dioxide.

There were therefore 350·3 c.c. of carbon dioxide in the medium and 111·3 c.c. evolved as gas, making a total of 461·6 c.c. Control experiments were made with the medium before inoculation, but no trace of carbon dioxide could be found. This gas can therefore only have been produced from the sodium formate.

The total amount of hydrogen produced was found to be 451·1 c.c.

Within the limit of experimental error, the ratio $CO_2 : H_2$ is therefore 1 : 1.

This leads us to the conclusion that these bacteria decompose sodium formate according to the equation:

$$H \cdot CO_2Na + H_2O = NaHCO_3 + H_2$$

or that the formic acid is decomposed thus :

$$H \cdot CO_2H = H_2 + CO_2.$$

This decomposition of formic acid is thus similar to that induced by platinum black or powdered ruthenium, iridium, or rhodium.

The use of such a medium as meat extract is open to the objection that it itself yields a small amount of gas. In subsequent experiments, we have therefore substituted for this medium a 2 per cent. solution of peptone in water. This, when inoculated with the various bacteria mentioned above, yields no trace of gas.

On inoculating the 2 per cent. solution of peptone after adding 0·5 per cent. of sodium chloride and varying percentages of sodium formate, vigorous evolution of gas occurs and the analytical examination of the gases produced gave results exactly similar to those described above in detail.

In estimating the amount of formate decomposed we have been unable to find any satisfactory method of determining the amount of formate present in the medium, we have therefore calculated the amount decomposed from the volume of hydrogen evolved. From this it seems that never more than from 25—30 per cent. of the formate present is decomposed: this certainly applies to proportions of from 0·2 to 2·0 per cent. of formate. Many of the bacteria will grow in media containing as much as 5 or even 10 per cent. of formate, but we have as yet made no estimations of the gases produced under these conditions.

Since the power of decomposing sodium formate might possibly serve as a useful means of diagnosis in the identification of bacteria, we have made some preliminary observations with a few of the better known organisms.

The following bacteria have given positive results :

The *B. coli communis* (80 different strains), *B. enteritidis* of Gärtner (2 strains), *Pneumobacillus* of Friedländer (2 strains), *B. lactis aerogenes* (2 strains), *B. cloacæ*, *B. choleræ gallinarum*, *Proteus vulgaris*, *B. prodigiosus*, and *B. rouge de Kiel.*

The following have failed to decompose the sodium formate :

B. typhi abdominalis (11 strains), *B. rhinoscleromæ*, *B. pyocyaneus* (2 strains), *B. denitrificans*, *B. anthracis* (2 strains), *B. subtilis*, *B. mesentericus vulgatus*, *B. mycoides*, *B. ramosus*, *B. arborescens*, *B. fluorescens non liquefaciens*, *B. janinthus*, *B. megatherium*, *B. buccalis maximus* *B. choleræ suis*, *Vibrio Metschnikovi*, *V. choleræ*, *Vibrio* of Finkler and Prior, *Vibrio* of Deneke, *Spirillum rubrum*, *Micrococcus cereus flavus*, *M. luteus*, *Staphylococcus aureus* (2 strains), *Staph. citreus*, *Staph. albus*, *Sarcina lutea*, *S. aurantia*, and all the common *Saccharomycetes.*

It will be observed that all the bacteria mentioned above which

produce gas from sodium formate also produce it from *d*-glucose, whilst those which do not produce gas from sodium formate do not produce it from *d*-glucose; the yeasts, however, it is important to note, do not produce gas from the formate, although they readily decompose *d*-glucose.

We are extending this work on the action of bacteria to other substances of a similar nature, and hope shortly to publish the results obtained with acetic and oxalic acids.

XLI.—*Preparation of Substituted Amides from the Corresponding Sodamides.*

By Arthur Walsh Titherley, M.Sc., Ph.D.

In a previous paper (Trans., 1897, 71, 460), the author drew attention to the behaviour of sodium acetamide, and other sodamide derivatives with alkyl haloids; and it was shown that the action was somewhat anomalous in the sense that it appeared difficult to bring about simple change. This observation has been confirmed by subsequent experiments, although, under favourable conditions, it has been found possible to bring about simple condensation in many cases. As it seemed important to ascertain these conditions, and to determine how far it was possible to apply the reactions for synthetical purposes, a series of experiments were carried out in order to effect a condensation between sodamide derivatives of the type R·CO·NHNa, and various halogen products. Of the latter, those which have been used are:

a. Alkyl haloids.
b. Acid chlorides.
c. Halogen-substituted esters.
d. Bromamides.

The action of the halogens, bromine and iodine, which was also examined in the attempt to imitate Spring's reaction, gave only very unsatisfactory results, owing to complex changes taking place, the nature of which has not been studied.

With *a*, *b*, and *c*, it has been found that, under suitable conditions, sodium derivatives of the aromatic amides in general behave normally, simple condensation taking place; for example:

$$C_6H_5\cdot CO\cdot NHNa + C_2H_5I = C_6H_5\cdot CO\cdot NH\cdot C_2H_5 + NaI.$$
$$C_6H_5\cdot CO\cdot NHNa + CH_3\cdot COCl = C_6H_5\cdot CO\cdot NH\cdot CO\cdot CH_3 + NaCl.$$

On the other hand, sodium derivatives of the aliphatic amides behave differently, yielding, as a rule, only small quantities (if anything) of direct condensation products, owing to unexpected bye

reactions which occur. The importance of this, in its bearing upon the difference in constitution between aliphatic and aromatic amides, will be discussed later.

A much easier and more convenient method of replacing the sodium atom in these sodium derivatives by alkyl groups, and thus of synthesising various alkyl-substituted amides, is by heating the sodamide with potassium alkyl sulphates, when the following change occurs:

$$R\cdot CO\cdot NHNa + KR^1SO_4 = R\cdot CO\cdot NHR^1 + KNaSO_4.$$

This method has the advantage of simplicity, and is applicable equally to fatty as well as to aromatic amides. During the course of this investigation, it has been considerably used in the preparation of monoalkyl-, as well as simple and mixed dialkyl-acetamides and -benzamides.

Sodium derivatives of monoalkyl amides, $R\cdot CO\cdot NNaR^1$, have been obtained by the action of sodamide, which reacts similarly to simple amides, although less readily, ammonia being disengaged thus:

$$R\cdot CO\cdot NHR^1 + NaNH_2 = R\cdot CO\cdot NNaR^1 + NH_3.$$

I. Syntheses with Halogen Organic Compounds.

Action of Alkyl Iodides on Sodamierde Divatives.

When sodium acetamide, sodium benzamide, &c., suspended in benzene (in which they are slightly soluble), are heated with methyl or ethyl iodide, ethylene dibromide, &c., no reaction takes place. In presence of alcohol, however, a steady action sets in, with continual formation of sodium iodide or bromide, and after a few hours boiling the change is complete, and the reaction neutral. As organic sodamides are quite stable in the presence of alcohol (Trans., 1897, 71, 467), it was thought at first that a change must have occurred between the sodium derivative and the alkyl haloid, for instance:

$$CH_3\cdot CO\cdot NHNa + CH_3I = CH_3\cdot CO\cdot NH\cdot CH_3 + NaI.$$

On working up the product, however, it was found that simply acetamide, and not the methyl derivative (in this case), had been formed. This was found to be true with other alkyl haloids, that is, in all cases, when alcohol was used, acetamide was formed. Obviously, therefore, alcohol takes part in the reaction, and it was subsequently proved that an ether is produced, which in the earlier experiments passed off undetected; thus:

$$CH_3\cdot CO\cdot NHNa + CH_3I + C_2H_5\cdot OH = CH_3\cdot CO\cdot NH_2 + NaI + CH_3\cdot O\cdot C_2H_5.$$

This was shown to be the case by varying the alcohol and alkyl

haloid in different experiments. For instance, in one case, in allowing benzyl chloride to act on sodium acetamide dissolved in ethyl alcohol; the reaction went very readily, giving an excellent yield of acetamide and benzyl ethyl ether.

In a series of experiments with ethylene dibromide, the result was curious; large volumes of vinyl bromide were evolved, whilst the alcoholic residue, after decanting from the separated sodium bromide, yielded a peculiar double compound of the latter with acetamide (compare this vol., p. 413). In presence of boiling benzene, no action occurs, and hence, in this case, the alcohol must act as a carrier, although not itself changed.

$$CH_3{\cdot}CO{\cdot}NHNa + CH_2Br{\cdot}CH_2Br = CH_3{\cdot}CO{\cdot}NH_2 + NaBr + CH_2{:}CHBr.$$

Attempts were then made to effect the change in absence of alcohol at moderately high temperatures in a sealed tube, with the result that a marked difference became apparent between the aliphatic and aromatic sodamides. Whereas the latter condense readily with alkyl iodides at 140°, forming substituted alkylamides, aliphatic sodamides react only with difficulty, forming comparatively small quantities of alkyl derivatives, bye reactions taking place. The two following experiments serve as types to show this.

Action of Ethyl Iodide on Sodium Acetamide at 150°.—Fifteen grams of the sodium compound and 30 grams of ethyl iodide were heated in a sealed tube at 150° for an hour. The product of the change which was dark contained granular sodium iodide, and a mobile oil (10 grams) boiling at 80°, which proved to be unchanged ethyl iodide. After removing this, the contents of the tube were extracted with a mixture of alcohol and benzene (the latter to prevent, as far as possible, the sodium iodide from dissolving). The oil which was extracted was then fractionated; it boiled at 118° under 30 mm. pressure, and on standing partly separated as crystals, melting at 81° (acetamide), the total weight of which was 1¼ grams. The liquid portion was now carefully fractionated; it boiled chiefly between 200° and 205°, giving an oil consisting essentially of acetethylamide, which was further purified by another fractionation (203—205°). It was identical with the product previously described by Wurtz, boiling at 205°, but the total yield was barely 3 grams.

A large number of experiments made with ethylene dibromide, methyl iodide, and other alkyl iodides in sealed tubes gave similar results, unsatisfactory on account of the small yields, and in some cases acetamide itself seemed to be the chief product. It therefore appears that the method cannot be conveniently used for synthetical purposes.

Action of Ethyl Iodide on Sodium Benzamide at 140°.—Fourteen grams

of sodium benzamide (moist with benzene) and 15 grams of ethyl iodide were, in one experiment, heated together in a sealed tube at 140° for 1—2 hours. After cooling, the contents of the tube were found to be in two layers; the one (smaller), clear and mobile, consisted of benzene with a little unchanged ethyl iodide, the other was a brownish oil mixed with sodium iodide. This was treated with water, and the oil, which on standing commenced to crystallise, was extracted with ether and fractionated at the ordinary pressure.

Three fractions were obtained as clear, colourless oils, namely:

A boiling at 250—260°. C boiling at 280—290°.
B „ 260—280.

These fractions, however, were practically identical, and on standing began to crystallise in large, flat, cross-twinned plates, melting at 68°, and after several recrystallisations at 71°. The total yield of the substance, which was benzethylamide, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_2H_5$, was about 12 grams or 60—70 per cent. of the theoretical.

The fractions A, B, and C, however, did *not entirely* solidify. On the contrary, a thick oil remained which, when drained from the crystals, showed no signs of solidifying after several months. At first this oil was thought possibly to be a diethyl derivative, but on analysis it proved to be the monoethyl compound:

0·1752 gave 14·0 c.c. moist nitrogen at 14° and 746 mm. N = 9·23.
$C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_2H_5$ requires N = 9·39 per cent.
$C_6H_5{\cdot}CO{\cdot}N(C_2H_5)_2$ „ N = 7·91 „

The amount of this liquid was only small, being about 10 per cent. of the total yield. The oil and the ordinary solid benzethylamide were next separately fractionated. Their boiling points were practically identical.

B. p. of (α) solid product was 285° at 750 mm.*
„ (β) liquid „ 282—285° at 750 mm.

Since, before separation, the products come over with a gradual rise of the thermometer from 250—290°, it seems probable that we are dealing here with a true mixture, and that therefore the β-liquid form is some isomeric modification of benzethylamide.

Similar experiments with other alkyl iodides gave successful results, and thus it is clear that the method may be applied to the aromatic amides in the preparation of their substitution derivatives.

Phenyl iodide or chloride has no action on sodium acetamide or sodium benzamide in presence of alcohol, or even in a sealed tube at 230°.

* Schmidt and Gattermann (*Annalen*, 1888, **244**, 50) give the boiling point of benzethylamide as 256—260°, whilst Wheeler and Johnson (*Amer. Chem. J.*, 1899, **21**, 185) give it as 298—299°.

Action of Acid Chlorides on Aromatic Sodamides.

These react in benzene solution with great ease, forming secondary amides, for example:

$$C_6H_5{\cdot}COCl + C_6H_5{\cdot}CO{\cdot}NHNa = (C_6H_5{\cdot}CO)_2NH + NaCl.$$

The yields are fairly good, and secondary changes are small, provided the acid chlorides taken are tolerably pure and free from hydrochloric acid; the reaction forms a ready general method of preparation of secondary amides. The preparation is very simple, and in general may be conducted as described in the case of the following typical examples.

Dibenzamide.—Nine grams of benzamide in 200 grams of benzene were treated with 3 grams of powdered sodamide, and boiled until all the ammonia was expelled. The white sodium benzamide thus obtained was then treated with 10·4 grams of benzoyl chloride mixed with 20 grams of benzene.

The reaction was energetic and the mixture grew hot; to complete the change it was heated for 4 hours, by which time it was neutral to litmus. About 6 grams of salt separated, and after filtering this off and concentrating the solution, stellate clusters of long, white needles were deposited, and a further crop of crystals were obtained from the mother liquor by adding light petroleum. The yield was 9 grams, and on recrystallising from alcohol the product melted at 148°, and was in every way identical with dibenzamide.

0·2571 gave 14·0 c.c. moist nitrogen at 16° and 757 mm. N = 6·31.
$C_{14}H_{11}O_2N$ requires N = 6·22 per cent.

No action occurs between benzamide (free) and benzoyl chloride.

Acetylbenzamide is readily formed by the action of acetyl chloride on sodium benzamide, but not (*loc. cit.*) from benzoyl chloride and sodium acetamide. The proportions taken were 9 grams of benzamide, 3 grams of sodamide in 200 grams of benzene, and (after driving off the ammonia) 5·8 grams of acetyl chloride. As in the previous case, the action is energetic and heat is liberated. The change was completed by boiling for 6 hours. Owing to the presence of a little free acid in the acetyl chloride, some free benzamide is usually formed, most of which separates from the benzene filtrate on standing. On evaporation and careful crystallisation from chloroform, somewhat discoloured needles were obtained which, after draining on a porous plate and twice recrystallising from alcohol, separated as long, white prisms melting as 117°.

0·101 gave 7·4 c.c. moist nitrogen at 9° and 750 mm. N = 8·54.
$C_9H_9O_2N$ requires N = 8·58 per cent.

Action of Acid Chlorides on Aliphatic Sodamides.

A marked difference is here noticeable between aliphatic and aromatic amides. Sodium acetamide, for example, although it reacts simply and normally with acetyl chloride giving diacetamide, behaves very differently with benzoyl chloride.

Diacetamide may be obtained by the action of free acetamide on acetyl chloride (compare this vol., p. 411). It is also readily obtained from the sodium derivative. Seven grams of sodium acetamide (prepared from acetamide and sodamide) were suspended in 50 grams of benzene, and gradually treated with 7·8 grams of pure acetyl chloride. The reaction, which is vigorous, was completed by boiling for an hour, after which the white mass of separated sodium chloride was filtered from the hot benzene solution. The latter, on cooling, deposited some crystals melting at about 132°, which proved to be acetamide hydrochloride, and after removing this and distilling off the benzene, a residue was obtained which, on fractionation, boiled at 212—215°. The distillate on cooling immediately set to a fine white, stellate mass which, on crystallisation from benzene and light petroleum, melted at 78°. The yield was about 4 grams.

0·1018 gave 12·2 c.c. moist nitrogen at 16° and 748 mm. N = 13·74.
$C_4H_7O_2N$ requires N = 13·86 per cent.

Action of Benzoyl Chloride on Sodium Acetamide.—It was at first expected that the result of this action would be identical with that of acetyl chloride on sodium benzamide, namely, acetylbenzamide. In no case, however, was any trace of the latter isolated after the reaction, although this substance is well defined and easily identified. On the contrary, everything pointed to a complex change of some kind having occurred. In order to ascertain the course of the reaction, a number of experiments were carried out in presence of benzene, using 1 mol. of sodium acetamide and 1 mol. of benzoyl chloride. After completing the reaction, which is energetic, by heating until neutral, thick masses of sodium chloride separated, and were filtered off from the hot benzene solution. The filtrate, on evaporation, left a thick oil which solidified incompletely and very slowly. The solid portion which crystallised out melted at 148° after purification, and was *dibenzamide*. On treatment of the remaining oily mass with cold dilute caustic potash, more dibenzamide, which was present, was removed (as its soluble potassium derivative) along with a quantity of *benzoic acid*, *acetamide*, *diacetamide*, and *sodium acetate*, which were present. The portion insoluble in alkali was oily and semi-solid, and was fractionally crystallised from benzene. The first needle tufts of silky crystals which were got melted at 190°, and

on subsequent purification at 201°, and had all the properties of *tribenzamide* (Curtius, m. p. 202°).

Next, a crop of small plates was obtained which, after purification melted at 128° (*benzamide*). The mother liquor from these, which would not solidify even in a vacuum, was then distilled; an oil came over at 187—190° which was *benzonitrile*, and finally at very much higher temperatures, about 350°, a yellowish oil was collected which solidified on standing, and on crystallising from chloroform, formed long, white prisms melting at 45°. This proved to be simply *benzoic anhydride*.

The change which takes place, therefore, is obviously very complex, and is probably (inadequately) expressed by the equations:

$$2C_6H_5\cdot COCl + NaNH\cdot CO\cdot CH_3 = (C_6H_5\cdot CO)_2NH + (CH_3\cdot CO)_2NH + 2NaCl.$$

$$4C_6H_5\cdot COCl + 4NaNH\cdot CO\cdot CH_3 = (C_6H_5\cdot CO)_3N + (CH_3\cdot CO)_3N + C_6H_5\cdot CO\cdot NH_2 + CH_3\cdot CO\cdot NH_2 + 4NaCl.$$

$$C_6H_5\cdot COCl + 2NaNH\cdot CO\cdot CH_3 = C_6H_5\cdot CN + CH_3\cdot CO_2Na + CH_3\cdot CO\cdot NH_2 + NaCl.$$

$$2C_6H_5\cdot COCl + 2NaNH\cdot CO\cdot CH_3 = (C_6H_5\cdot CO)_2O + CH_3\cdot CO\cdot NH_2 + CH_3\cdot CN + 2NaCl.$$

Of the different products which were isolated, dibenzamide appears to be formed in perhaps the greatest quantity.

The explanation of the difference in the behaviour of sodium acetamide and sodium benzamide probably lies in a difference in the constitution of these compounds, and therefore possibly of aliphatic and aromatic amides.

Action of Halogen Derivatives of Esters.

Owing apparently to their more negative character, halogen-substituted esters, such as ethyl chloroacetate and ethyl chlorocarbonate, react more readily than alkyl haloids with sodium acetamide and sodium benzamide, but here also the yields are poor owing to complex bye reactions occurring. Alcohol cannot be used as a menstruum, since it takes part in the change as in the case of alkyl haloids, but in presence of benzene, direct condensation may be effected. Only a few experiments in this direction have been carried out, as they were very unpromising from a synthetical point of view, and only in the case of aromatic amides were any successful results obtained. The following synthesis of ethyl hippurate is an example.

Action of Ethyl Bromoacetate on Sodium Benzamide.—The change is simple:

$$C_6H_5\cdot CO\cdot NHNa + BrCH_2\cdot CO_2\cdot C_2H_5 = C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot CO_2\cdot C_2H_5 + NaBr.$$

Twenty grams of benzamide by treatment with 6·6 grams of sodamide in presence of benzene, were converted into sodium benzamide which, after cooling, was treated gradually with 28 grams of ethyl bromoacetate. The reaction commenced in the cold, and the mixture became brownish. It was boiled for 2 to 3 hours, until neutral, after which the benzene was distilled off, and the residue extracted with alcohol. From the alcoholic solution, along with benzamide and benzoic acid, ethyl hippurate was obtained as fine needles which, on hydrolysis with alcoholic potash and subsequent acidification, yielded hippuric acid melting at 185—186°. The yield was only 6 grams, but the synthesis is of interest.

Action of Bromamides on Sodamide Derivatives.

The bromamides of the type R·CO·NHBr, described by Hofmann, are fairly stable, well defined compounds, soluble in benzene, alcohol, &c., and very reactive. Their behaviour with sodamide derivatives was studied with a view of attempting to synthesise hydrazine compounds by a change represented by the equation

$$R{\cdot}CO{\cdot}NHBr + NaNH{\cdot}CO{\cdot}R = R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}R.$$

The results were entirely negative, although interesting. In spite of all attempts to prevent it, molecular rearrangement invariably took place during the reaction with the formation of a urea derivative of the type $CO<^{NH\cdot R}_{NH\cdot CO\cdot R}$. A short description of two examples will serve to show how the experiments were carried out.

Action of Acetbromamide on Sodium Acetamide.—Six grams of pure acetbromamide (1 mol.) and 3·6 grams of sodium acetamide (1 mol.), each separately dissolved in 16 grams of absolute alcohol, were mixed and the solution gently warmed. Sodium bromide began to form immediately. After heating for about an hour, the liquid was neutral to litmus, and was then treated with benzene to completely separate the sodium bromide which was filtered off. The filtrate, on evaporation and standing, deposited fine, colourless needles, half an inch long, in beautiful twinned tufts. After recrystallising, this substance melted at 178° and was in every respect identical with *a-b*-methylacetylurea, NHMe·CO·NHAc, (m. p. 180°; Hofmann, *Ber.*, 1881, 14, 2725). In other experiments, where benzene instead of alcohol was used as the menstruum, in a sealed tube at 120—130°, the same product was obtained, without any indication of the formation of an isomeric hydrazine derivative.

Action of Benzoylbromamide on Sodium Benzamide.—On warming the substances together in presence of alcohol or of benzene, a ready action set in with the separation of sodium bromide, and the filtrate, on evaporation and cooling, deposited a fine, white, crystalline mass which,

when recrystallised from benzene, yielded a small quantity of plates melting at 128° (benzamide), but chiefly needles melting at 200°, and after further purification at 203°. The latter product proved to be identical with *a-b*-phenylbenzoylurea, NHPh·CO·NHBz (m. p. 204°, *Ber.*, 1884, **17**, 2881). No evidence of the formation of symmetrical dibenzoylhydrazine could be obtained.

It is of interest in this connection to note that Blac er (*Ber.*, 1895, **28**, 432), by the action of iodine on sodium benzamide, obtained *a-b*-phenylbenzoylurea, and not the expected hydrazine derivative.

II. Syntheses with Potassium Alkyl Sulphates.

Preparation of Amines from Sodamide.

It has previously been pointed out (Trans., 1894, **65**, 521) that all attempts to bring about the interaction of alkyl haloids and sodamide, with a view of preparing amines by the possible change $RI + NaNH_2 = RNH_2 + NaI$, were met with failure. Either no reaction takes place, or a violent one occurs, accompanied by complex decomposition and charring.

It is interesting therefore, in this connection, to find that aliphatic amines can be prepared from sodamide by using potassium alkyl sulphates.

Ethylamine.—When sodamide (moist with benzene) is intimately ground with *anhydrous* potassium ethyl sulphate, and the mixture heated gradually to 180—200°, an energetic action sets in with steady evolution of ethylamine (admixed with some ammonia). The gaseous products may be absorbed by hydrochloric acid, the solution evaporated, and ethylamine hydrochloride extracted by alcohol as usual. The change is essentially:

$$NaNH_2 + K\cdot C_2H_5SO_4 = NaKSO_4 + C_2H_5\cdot NH_2.$$

It is quite general, and the author has employed it by using various potassium alkyl sulphates in the preparation of several primary aliphatic amines, such as methylamine, butylamine, &c.

Preparation of Alkyl-substituted Amides.

Further, the reaction applies, not only to sodamide, but in a wide sense to its derivatives. Most of the experiments so far have been applied to derivatives of organic amides of the type R·CO·NHNa, already dealt with in the previous portion of this paper, especially of acetamide and benzamide.

It should be noted that Blacher (*Ber.*, 1895, **28**, 2352) has already shown that sodium benzamide and sodium phthalimide, when heated with potassium ethyl sulphate, give the corresponding ethyl derivatives

The previous methods of preparation of alkyl-substituted amides of the type $R{\cdot}CO{\cdot}NHR^1$ and $R{\cdot}CO{\cdot}NR^1_2$, are (1), the action of cyanic esters upon acids and anhydrides, a method discovered by Wurtz, and (2), the action of amines on acid chlorides or esters. From want of convenience, or owing to other difficulties with either of these methods, comparatively few substituted amides and their derivatives, and no mixed compounds, appear to have been obtained, and it was therefore thought desirable to test the applicability of the potassium alkyl sulphate reaction. The results have been in every way satisfactory, and the reaction forms the basis of a ready general method of synthesis, which has the advantage of affording a direct means of introducing any desired alkyl into the amido-group, $CO{\cdot}NH_2$, giving first monosubstitution, and then by a second stage, disubstitution derivatives. As yet only a few of the latter have been thus obtained.

The stages showing the successive changes may be represented thus:

$R{\cdot}CO{\cdot}NH_2$, with sodamide or sodium ethoxide $\longrightarrow$ $R{\cdot}CO{\cdot}NHNa$

$R{\cdot}CO{\cdot}NHR^1$, with sodamide $\longrightarrow$ $R{\cdot}CO{\cdot}N{<}^{R^1}_{Na}$

(with KR^1SO_4 at 180—200°)

(with KR^2SO_4 at 180—200°)

$R{\cdot}CO{\cdot}N{<}^{R^1}_{R^2}$, where R^1 and R^2 may be similar or dissimilar alkyl radicles.

The potassium alkyl sulphates were prepared in quantity, from their respective alcohols (primary only) by the usual method, care being taken to ensure that they were perfectly anhydrous. Several contain water of crystallisation, and were dried at 120—130°.

Monoalkyl-substituted Amides.

The interaction of the sodamide derivative (for example, sodium acetamide) and potassium alkyl sulphate, which readily takes place on heating, may be brought about in one of two ways, namely:

Method A.—Direct distillation at a temperature sufficient to distil over the product formed—in the case of higher homologues under reduced pressure—the distillate being subsequently fractionated.

Method B.—Heating at 180—200°, in a bath of oil or sulphuric

acid, in a flask provided with an upright condenser tube, which is a necessary precaution, since the reaction is generally sufficiently energetic to cause rapid vaporisation of even products of high boiling point. The contents of the flask soften, and in about 20 minutes become semi-liquid, owing to formation of an alkylamide. The latter is subsequently extracted by boiling benzene, and after filtering on the pump, and removing the benzene by distillation, the product is fractionated.

The sodium derivative, $NaNH{\cdot}CO{\cdot}R$, may be obtained from the organic amide by the action of sodamide, or, more conveniently, sodium ethoxide in presence of alcohol, since the sodium compound need not be isolated, and alcohol does not interfere with the reaction. The procedure is then as follows.

Sodium (1 at.) is dissolved in the minimum quantity of alcohol in a capacious distilling flask, treated with benzamide or acetamide (1 mol.) suspended in a little alcohol, and the whole well shaken and warmed for a few minutes. Finely-powdered potassium alkyl sulphate (1 mol.) is then added, and the mixture well incorporated by shaking or otherwise. After removing the alcohol by distillation, the intimate mixture is either carefully distilled, or treated as in B.

In this way, methyl, ethyl, propyl, and butyl derivatives of acetamide and benzamide have very easily been prepared. Some of these appear not to have been obtained hitherto.

Acetmethylamide, $CH_3{\cdot}CO{\cdot}NH{\cdot}CH_3$, already prepared by Hofmann (*Ber.*, 1881, **14**, 2729), was obtained in very deliquescent needles melting at 28°.

Acetethylamide, $CH_3{\cdot}CO{\cdot}NH{\cdot}C_2H_5$, also obtained by Wurtz (*Annalen*, 1850, **76**, 334; 1853, **88**, 315), was prepared by method A. The product, after fractionation, was found to contain some acetamide, which was removed by shaking with strong caustic potash solution. Pure acetethylamide floated on top (although readily soluble in water) as an oil which was extracted by ether. It boiled at 204—205°, and the yield of pure product was 9 grams from 11·8 grams of acetamide.

Acetethylamide absorbs hydrogen chloride rapidly, becoming hot, and from the thick liquid thus formed, the *hydrochloride* slowly crystallises, on cooling, if anhydrous in stellate growths of fine, white, very deliquescent needles melting at about 60°. A weighed portion was analysed by dissolving in water, and after neutralising with sodium hydroxide, titrated with silver nitrate. The base and acid were found to be present in the salt in molecular proportion (compare acetamide hydrochloride).

0·1652 required 14·0 c.c. $N/10$ $AgNO_3$. $HCl = 30·26$.

$CH_3·CO·NH·C_2H_5,HCl$ requires $HCl = 29·55$ per cent.

Sodium Acetethylamide, $CH_3·CO·NNa·C_2H_5$, was obtained by the action of finely-powdered sodamide, in presence of a little benzene, on the base. The mixture grew warm and ammonia was evolved; but the action is not so energetic as that of sodamide upon acetamide, owing to the more basic nature of the alkyl derivative. The reaction was completed by heating gently till the evolution of ammonia ceased, after which the granular precipitate was washed with benzene and dried in a vacuum.

It was thus obtained as a white powder, which dissolves in alcohol, apparently without decomposition, since with alcoholic silver nitrate the solution gives an orange precipitate, which, however, quickly darkens, and is probably *silver acetethylamide*. It was much too unstable for analysis. The sodium compound, with a little water, is at once decomposed, liberating free acetethylamide as an oil, which dissolves on adding more water.

Acet-n-*propylamide*, $CH_3·CO·NH·C_3H_7$, has been described by Chancel (*Compt. rend.*, 1894, 119, 233) as a liquid boiling at 222—225°. It is easily obtained by method A as an oil boiling at 222° under 760 mm. pressure, and is miscible with water. The aqueous solution is precipitated by strong caustic potash or soda. Like acetethylamide, it is hydrolysed much more readily by concentrated hydrochloric acid than by alkali.

Acet-n-*propylamide Hydrochloride*, $CH_3·CO·NH·C_3H_7,HCl$, is formed similarly to the corresponding ethyl derivative. A thick liquid is produced, which solidifies slowly to a mass of deliquescent, white needles melting at about 47°.

Sodium Acet-n-*propylamide*, $CH_3·CO·NNa·C_3H_7$, is obtained by the action of sodamide upon the base, ammonia being evolved. In presence of benzene it forms a thick, gelatinous solid, drying to a fine, white powder similar in its properties to sodium acetethylamide.

*Acetiso*butylamide, $CH_3·CO·NH·C_4H_9$, 19·6 grams of acetamide, 7·6 grams of sodium dissolved in the minimum quantity of alcohol, and 64 grams of potassium *iso*butyl sulphate were taken. The distillate on fractionation gave a small quantity of a volatile solid (which was not investigated), and a product boiling at 80—105°, consisting of alcohol and a little *iso*butyl alcohol, whilst the remainder came over at about 222°. This weighed 12·5 grams, and contained some acetamide, which was removed by shaking with cold caustic potash solution, the insoluble

oil being extracted and distilled. It boiled at 225—227° under 745 mm. pressure, and the yield of pure product was 8·5 grams.

0·1905 gave 20·9 c.c. moist nitrogen at 14° and 757 mm. N = 12·35.
$C_5H_{13}ON$ requires N = 12·17 per cent.

Acet*iso*butylamide is a colourless liquid having a faint basic smell slightly resembling that of acetamide. It is miscible with water in all proportions, but the aqueous solution is at once precipitated by weaker solutions of alkali than are necessary in the case of lower homologues. When boiled with strong potash or soda, it slowly undergoes hydrolysis, giving *iso*butylamine, and the same change is effected more readily by aqueous hydrochloric acid.

Acetisobutylamide Hydrochloride, $CH_3{\cdot}CO{\cdot}NH{\cdot}C_4H_9,HCl$.—When an ethereal solution of the base is treated with dry hydrogen chloride, an oil immediately separates which quickly solidifies to a mass of white plates melting at 107° without decomposition. In the absence of ether, the same substance is formed, the gas being rapidly absorbed with considerable rise of temperature. The increase in weight was ascertained, in one experiment, to be 30·17 per cent. (calculated 31·62 per cent.). On analysis:

0·5649 required 36·7 c.c. *N*/10 $AgNO_3$. HCl = 23·71.
$C_5H_{13}ON,HCl$ requires HCl = 24·04 per cent.

Sodium Acetisobutylamide, $CH_3{\cdot}CO{\cdot}NNa{\cdot}C_4H_9$, is formed by the action of sodamide on the free base, with evolution of ammonia and a little *iso*butylamine, as a slightly discoloured, thick jelly in the presence of benzene, in which it is appreciably soluble.

Benzmethylamide, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_3$, has been described by Romburgh (*Rec. trav. Chim.*, 1885, **4**, 388) as a solid melting at 79°; the boiling point was not given. Prepared by method A or B, it was obtained as large, colourless plates melting at 80—81°, and boiling without decomposition at 291° under 765 mm. pressure.

Sodium Benzmethylamide, $C_6H_5{\cdot}CO{\cdot}NNa{\cdot}CH_3$, is formed readily by the action of sodamide, as in the case of the ethyl derivative (*loc. cit.*). It is a white, granular powder, decomposed immediately by water, giving benzmethylamide.

Benzethylamide, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_2H_5$, was described by Romburgh (*loc. cit.*), and by Gattermann and Schmidt (*Annalen*, 1888, **244**, 50) as a solid, melting at 67° and boiling at 250—260°. Prepared by method A or B, it was obtained as fine, large, rectangular plates, forming characteristic cross-twinned combinations, the form being apparently rhombic. When recrystallised, it melted at 71°, and boiled at 285°

under 745 mm. pressure. In its preparation by method A, 15 grams of benzamide and 2·8 grams of sodium, each dissolved in the minimum quantity of alcohol, were mixed and treated with 20 grams of potassium ethyl sulphate, the alcohol driven off, and the mixture gently distilled. The distillate, on fractionation, gave the following products:

(1) At 78°, alcohol.

(2) Below 200°, a liquid, about 2 grams, chiefly benzonitrile.

(3) 200—260°, 3 grams, mixture of benzonitrile and benzethylamide.

(4) 260—285° (chiefly 285°), 11·5 grams, benzethylamide.

Fraction (4) came over as a thick, nearly colourless oil, which quickly began to solidify in large plates. As in the case of the ethyl iodide synthesis, however, it never entirely solidified, but on draining and pressing on bibulous paper, yielded a liquid boiling at 283°, which possessed similar properties to solid benzethylamide.

By fractionating (3) again, a further quantity of benzethylamide was obtained, bringing the total yield to about 13 grams. By employing method B, which is slower, a somewhat better yield was obtained. The recrystallised substance was analysed:

0·1546 gave 12·7 c.c. moist nitrogen at 12° and 745 mm. N = 9·55.
$C_9H_{11}ON$ requires N = 9·39 per cent.

Benzethylamide Hydrochloride, $C_6H_5\cdot CO\cdot NH\cdot C_2H_5,HCl$.—The aromatic alkyl amides, like the aliphatic, form hydrochlorides containing acid and base in molecular proportion, but they are not so stable or well defined. They dissociate on heating, and gradually lose hydrogen chloride, even on standing in a vacuum over sodium hydroxide, a circumstance which points to the less basic nature of aromatic as compared with aliphatic alkyl amides.

When benzethylamide in ethereal solution is treated with dry hydrogen chloride, the hydrochloride is immediately precipitated as a thick oil which does not solidify on standing. In absence of ether, the base absorbs the gas slowly, and the crystals immediately commence to liquefy, ultimately forming a thick, viscid liquid. The increase in weight, which was ascertained, corresponds to that required for the above formula. When treated with water, the liquid becomes opaque and is decomposed, forming free benzethylamide, which soon crystallises as needles, and hydrochloric acid, which was determined as usual.

0·2422 required 13·2 c.c. *N*/10 $AgNO_3$. HCl = 19·89.
$C_9H_{11}ON,HCl$ requires HCl = 19·67 per cent.

Sodium Benzethylamide, $C_6H_5\cdot CO\cdot NNa\cdot C_2H_5$.—Sodamide, when heated in benzene solution with benzethylamide, brings about replacement of the aminic hydrogen by sodium with disengagement of ammonia:

$$NaNH_2 + C_6H_5\cdot CO\cdot NH\cdot C_2H_5 = C_6H_5\cdot CO\cdot NNa\cdot C_2H_5 + NH_3.$$

The reaction is not nearly so brisk as with benzamide, owing, no doubt, to the more basic nature of the ethyl derivative; indeed, it is almost impossible to complete it in presence of more than a very little benzene. The sodium compound separates as a fine, white, granular powder, which is appreciably soluble in benzene. After drying in a vacuum, it was analysed:

0·3719 gave 0·051315 Na. Na = 13·79.

$C_9H_{10}ONNa$ requires Na = 13·45 per cent.

This product, and other similar sodium alkyl benzamides are best prepared in presence of sufficient benzene only to prevent access of moisture, namely, by grinding together the calculated quantities of alkyl amide and sodamide (moist with benzene), and then gently heating in a flask on a sand-bath. Ammonia is given off in large quantity, and when it slackens, benzene is poured into the flask, and the whole well boiled for 2 or 3 hours, after which the solid compound is filtered on the pump, and washed well with boiling benzene.

Benz-n-*propylamide*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_3H_7$.—24·2 grams of benzamide, 4·6 grams of sodium dissolved in alcohol, and 35·6 grams of potassium *n*-propyl sulphate were used, the preparation being conducted similarly to that of benzethylamide. The distillate on fractionation gave, below 200°, about 2·5 grams of benzonitrile, after which the thermometer rose fairly rapidly to 290—296°, when the propyl derivative came over as an oil of a yellowish colour, owing to slight decomposition. Its weight was 13 grams, and a further 3 grams were obtained by redistilling the fraction between 200° and 290°.

The oil quickly set to a crystalline mass of fine, feathery plates. On draining on a porous plate, and recrystallising from alcohol or benzene, it slowly separated in large, diagonally marked, apparently cubic crystals, melting not very sharply about 82°. After several crystallisations from benzene and light petroleum, from which it separated in white, glistening plates, and finally from alcohol, it melted sharply at 84·5°.

0·3309 gave 24·7 c.c. moist nitrogen at 12° and 750 mm. N = 8·74.

$C_{10}H_{13}ON$ requires N = 8·58 per cent.

Benz-*n*-propylamide boils with very slight decomposition at 294—295° under 750 mm. pressure. It is slightly soluble in hot water, from which, on cooling, it separates as an oil which crystallises at once on shaking. It has distinct basic properties, and is fairly soluble in concentrated hydrochloric acid, but the solution is precipitated by adding water.

Benz-n-*propylamide Hydrochloride*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_3H_7$, HCl, is formed

as a very viscous, colourless liquid by the action of hydrogen chloride, as with benzethylamide. It dissociates in a vacuum or on heating.

0·1735 gave 0·0296 HCl. HCl = 17·06.
$C_{10}H_{13}ON$,HCl requires HCl = 18·29 per cent.

Sodium Benz-n-propylamide, $C_6H_5 \cdot CO \cdot NNa \cdot C_3H_7$, is a white, granular powder obtained by the action of sodamide upon the base, as in the case of ethyl derivative.

*Benziso**butylamide*, $C_6H_5 \cdot CO \cdot NH \cdot C_4H_9$.—Forty grams of benzamide, 7·6 grams of sodium, and 64 grams of potassium *iso*butyl sulphate were used, the preparation being conducted as in the previous cases. It is preferable to use method B, as by the distillation method there is considerable loss by charring. On fractionating the product under reduced pressure, a yellowish oil was obtained which, on standing, set to a crystalline mass of long cross-twinned needles; these were drained, and crystallised from benzene, chloroform, and finally from 80 per cent. alcohol. The substance separated as fine, white prisms melting when pure at 57°.

0·2839 gave 19·14 c.c. moist nitrogen at 13° and 745 mm. N = 7·81.
$C_{11}H_{15}ON$ requires N = 7·90 per cent.

Benz*iso*butylamide boils with slight decomposition at 295—296° under 760 mm. pressure, and has properties very similar to those of the lower homologues. It is soluble in concentrated hydrochloric acid, and is hydrolysed with difficulty.

It readily absorbs dry hydrogen chloride forming the *hydrochloride*, $C_6H_5 \cdot CO \cdot NH \cdot C_4H_9$,HCl, as a thick, viscous liquid which does not solidify.

With sodamide in presence of a little benzene, the base forms the sodium derivative, $C_6H_5 \cdot CO \cdot NNa \cdot C_4H_9$, as a jelly which on drying falls to a nearly white powder.

Dialkyl-substituted Amides.

A few dialkyl-substituted amides were obtained by the action of potassium alkyl sulphates on sodium alkyl amides thus:

$$R \cdot CO \cdot NNaR^1 + KR^2SO_4 = R \cdot CO \cdot NR^1R^2 + KNaSO_4.$$

The preparation was conducted as in the case of monoalkyl derivatives, except that alcohol and sodium ethoxide were not used in the formation of sodium derivatives of aromatic alkyl amides, $C_6H_5 \cdot CO \cdot NNaR$, since the latter are decomposed by alcohol. Hence, sodamide was used in their preparation, and benzene was always added during the mixing

with potassium alkyl sulphates, to prevent decomposition by moisture in the air.

In this way, one or two mixed dialkyl amides have been successfully prepared, but much more work in this direction remains to be done.

Acetmethylethylamide, $CH_3 \cdot CO \cdot N(CH_3) \cdot C_2H_5$, was obtained by the action of potassium methyl sulphate on sodium acetethylamide in molecular proportion. The reaction commences about 170°, and proceeds with some energy, but with evolution of a quantity of ethylamine and methylethylamine, showing that some bye-reactions occur. On distilling, a product came over which, by fractionation, was obtained pure as a light, colourless oil boiling at 180°.

It is miscible in all proportions with water, and has a peculiar basic smell and marked basic properties.

0·1121 gave 13·1 c.c. moist nitrogen at 10° and 755 mm. N = 13·90.
$C_5H_{11}ON$ requires N = 13·86 per cent.

Benzmethylethylamide, $C_6H_5 \cdot CO \cdot N(CH_3) \cdot C_2H_5$, was prepared from potassium methyl sulphate and sodium benzethylamide, obtained from sodamide as previously described. The mixture was heated in a sulphuric acid bath at 190—200° for 20 minutes. The mass softened owing to the formation of an oil which, on fractionation, boiled at 280°.

It is insoluble in water, but miscible with concentrated hydrochloric acid, the oil being precipitated again by adding water.

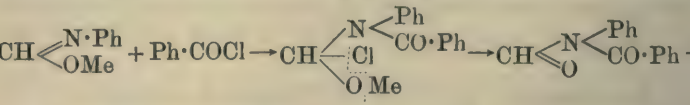
0·1940 gave 14·94 c.c. moist nitrogen at 15° and 747 mm. N = 8·87.
$C_{10}H_{13}ON$ requires N = 8·58 per cent.

III. Tautomeric Relations.

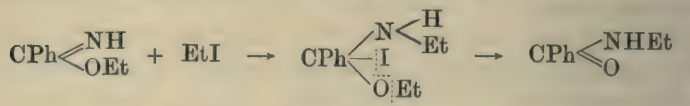
The question discussed in a previous paper (Trans., 1897, 71, 468) as to whether the metallic derivatives of organic amides are to be regarded as true sodamide compounds of the type $R \cdot CO \cdot NHNa$, or as salts of the tautomeric formula $R \cdot C{<}^{NH}_{ONa}$, is one on which, unfortunately, synthetical work can throw but little light. The fact that ethyl iodide, for instance, when heated with sodium benzamide, gives benzethylamide, in which there can be no doubt that the ethyl radicle is attached to nitrogen, cannot be accepted as an indication that the sodium atom must have been similarly attached, owing to the possible intermediate formation of additive compounds. There are, for example, independent reasons for believing that silver is attached to oxygen in silver anilides, yet these with acid chlorides, &c., give derivatives in which the group introduced is combined to nitrogen.

Wheeler and Walden (*Amer. Chem. J.*, 1897 '19, 129), working on the

imino-ethers (*iso*anilides), have shown that this addition and subsequent elimination takes place (in the case of methyl *iso*formanilide) thus:



Still more significant is the conversion of benzimino-ethyl ether into benzethylamide, by simply heating it to 100° with ethyl iodide:



Hence the production of benzethylamide from sodium benzamide and ethyl iodide may have taken place through the imino-ether phase, and so the result proves nothing regarding the constitution of the sodium compound. On the other hand, if the reaction could be effected in the cold, synthetical evidence would be of importance, since *white* silver benzamide treated in the cold with ethyl iodide yields benzimino-ethyl ether, pointing undoubtedly to the constitution $C_6H_5\cdot C\overset{NH}{\underset{OAg}{<}}$ for the silver derivative.

All attemps to effect syntheses in the cold with sodamide derivatives of the type R·CO·NHNa have failed except those with acid chlorides, which throw but little light on the reaction. The only conclusion that can be drawn with certainty is a recognition of a pronounced difference in the behaviour of aliphatic as distinguished from aromatic sodamide derivatives. That the difference is probably due to an actual difference in their structure is strengthened by other considerations, notably the following.

Alkyl iodides react fairly easily with aromatic sodamides, but with difficulty with aliphatic sodamides (giving only a small quantity of alkyl derivatives). This suggests a linking of metal to oxygen in the first, and to nitrogen in the second.

There are two silver derivatives of benzamide (see Trans., 1897, 71, 468), a white and an orange. The white is quite stable in presence of cold water, and as stated above is doubtless $C_6H_5\cdot C\overset{NH}{\underset{OAg}{<}}$. The orange variety, probably $C_6H_5\cdot C\overset{O}{\underset{NHAg}{<}}$, is very unstable, and quickly darkens and decomposes, rendering it impossible to ascertain its composition or structure.

When alcoholic silver nitrate is added *drop by drop* to an alcoholic solution of sodium benzamide, a curious result is obtained. An orange precipitate first forms, which contantly changes to white, until most

of the sodium benzamide has been precipitated. After this, further addition of silver nitrate produces a permanent orange precipitate, and this variety may be obtained by filtering at the right juncture, and adding silver nitrate to the filtrate.

With an alcoholic solution of sodium acetamide and silver nitrate, a bright orange precipitate only is obtained, but under certain conditions, namely, in presence of an excess of acetamide, an unstable, white compound is produced. An alcoholic solution of pure acetamide (in excess) is treated with a little sodium ethoxide, and on now adding silver nitrate, a white precipitate is formed, which, on standing or on adding a drop of water, turns bright orange. Unfortunately, this orange compound quickly darkens and decomposes, and so cannot be obtained pure for analysis. As it was considered important, however, to ascertain if it really is silver acetamide, and not a possible molecular compound of some kind, an attempt at analysis was made. A known quantity of sodium acetamide was obtained from a weighed quantity of sodium dissolved in alcohol and the equivalent quantity of acetamide, the solution being made up to a known volume. An aliquot portion was treated with a slight excess of alcoholic silver nitrate of known strength, and after filtering off the orange precipitate, the silver in the filtrate was determined.

0·1790 sodium acetamide required 0·2345 Ag. $76·35 = 100$ Ag.
$CH_3 \cdot CO \cdot NHNa$ requires $75·01 = 100$ Ag.

In another portion, the orange precipitate was filtered as quickly as possible, washed with alcohol and ether, and dried in a vacuum. During the operation, it became dark brown. On slightly warming, it decomposed with gentle explosion.

0·2704 gave 0·1882 Ag. Ag = 69·6.
$CH_3 \cdot CO \cdot NHAg$ requires Ag = 65·06 per cent.

The results are obviously only approximate, but they serve to indicate that the orange precipitate is really silver acetamide.

It must therefore be concluded that silver acetamide and silver benzamide exist in tautomeric forms, of which the white probably contains the structure $-C\lessdot^{NH}_{OAg}$, and the orange, $-C\lessdot^{O}_{NHAg}$.

Similarly, two corresponding sodium compounds may exist.

In the case of sodium benzamide in alcoholic solution, if the above reasoning is legitimate, we have essentially $C_6H_5 \cdot C\lessdot^{NH}_{ONa}$, with some $C_6H_5 \cdot C\lessdot^{O}_{NHNa}$ (probably in a condition of equilibrium), and this would account for its peculiar behaviour with silver nitrate, as well

as the ease with which the compound condenses with alkyl iodides, &c. (the sodium being attached to oxygen), as compared with sodium acetamide, in which, presumably, the form $CH_3 \cdot CO \cdot NHNa$ preponderates.

That more than one form of benzamide is capable of free existence is rendered improbable by an experiment in which an attempt was made to isolate such a compound from the white silver derivative, $C_6H_5 \cdot C \lessdot^{NH}_{OAg}$. The latter, suspended in dry ether, on decomposition by dry hydrogen sulphide, gave ordinary benzamide, and no indication of any isomeric substance. There is reason, however, to believe that, in aqueous solution at least, benzamide exists in the form of an imino-hydroxy-compound, since it shows distinct ionisation, whilst acetamide does not. Determinations, which were kindly undertaken by Dr. W. B. Davidson, at Aberdeen University, showed that the molecular conductivity, in aqueous solution at 25°, was:

Benzamide, $\mu_{64} = 1{\cdot}3$, $\mu_{1024} = 4{\cdot}2$.

Acetamide (middle fraction of a sample three times distilled), $\mu_{32} = 0{\cdot}95$.

This shows, as Ostwald observes, that acetamide is practically a non-conductor, and its molecule is doubtless $CH_3 \cdot CO \cdot NH_2$.

That the metallic compounds of acetamide are true sodamide derivatives, is further strengthened by the observations of Ley and Kissel (*Ber.*, 1899, **32**, 1357), who deduced from the low electric conductivity of mercury acetamide that the mercury atom is directly attached to nitrogen, inasmuch as they proved that all compounds, in which mercury is attached to oxygen, show a greater tendency to electrolytic dissociation. This confirms similar observations and deductions made by Kieseritzky (*Zeit. physikal. Chem.*, 1899, **28**, 385).

In regard to monoalkylamides, $R \cdot CO \cdot NHR^1$, the tautomeric form, $R \cdot C \lessdot^{N \cdot R^1}_{OH}$, may be capable of existence, isomeric also with $R \cdot C \lessdot^{NH}_{OR^1}$, which belongs to the class of well-known imino-ethers. No indication was obtained, in the foregoing work, of the existence of more than one type of alkylamide, except in the case already alluded to, of (β) liquid benzethylamide, which may possibly be an isomeric form; but this is very doubtful.

Attempts to prepare silver derivatives did not throw further light on the problem. Aliphatic alkylsodamides, $CH_3 \cdot CO \cdot NNaR$, in alcoholic solution, give orange *silver* derivatives with silver nitrate, but the corresponding aromatic compounds give a black precipitate, showthat these sodium derivatives are decomposed by alcohol, a fact which militates against the supposition that they are derivatives of the type

$C_6H_5\cdot C\lessdot^{N\cdot R}_{ONa}$. Attempts were made to prepare silver alkylbenzamides of this type by a method similar to that employed in the preparation of white silver benzamide (Trans., 1897, 71, 468), in order to study the action of alkyl iodides in the cold, with a view of synthesising dialkyl derivatives, $C_6H_5\cdot C\lessdot^{N\cdot R}_{OR}$, isomeric with dialkylamides; but entirely without success.

The potassium alkyl sulphate synthesis of mixed dialkyl amides may, by varying the order in which the alkyl groups are introduced, yield such isomeric derivatives, and further work in this direction is accordingly being carried out.

The instability of aromatic alkyl sodamides, $C_6H_5\cdot CO\cdot NNaR$, in presence of alcohol, as compared with aliphatic, also requires explanation, seeing that alkyl aliphatic amides are more basic. So also does the behaviour of acetamide, which, although in its relation with acids is more basic than benzamide, yet undoubtedly sustains substitution of its aminic hydrogen by sodium more readily than benzamide, either by treatment with sodamide or sodium ethoxide.

It is hoped that the extension of this work may help to further elucidate the peculiar relations that obtain between the amides of the aliphatic and aromatic series.

I desire to express my indebtedness to Professor J. Campbell Brown in kindly placing at my disposal the Research Laboratory of University College, Liverpool, where the above investigations have been conducted.

XLII.—*A New Method of Preparing Diacetamide.*

By Arthur Walsh Titherley, M.Sc., Ph.D.

It has been shown (this vol., p. 396) that diacetamide is formed by the simple reaction:

$$CH_3\cdot CO\cdot NHNa + CH_3\cdot COCl = (CH_3\cdot CO)_2NH + NaCl.$$

At the same time, the action of acetyl chloride on acetamide was studied. When these substances are mixed, an immediate change occurs, and a thick, white mass is formed without evolution of hydrogen chloride. On analysis, the white mass proved to be acetamide hydrochloride, which, with diacetamide, is formed thus:

$$3CH_3\cdot CO\cdot NH_2 + CH_3\cdot COCl = (CH_3\cdot CO)_2NH + (CH_3\cdot CO\cdot NH_2)_2,HCl.$$

The reaction, which takes place readily in presence of benzene, forms a convenient method of preparation of diacetamide, and may

be conducted as follows: 35·4 grams of acetamide (3 mols.) are placed in a large flask covered with 100 grams of benzene, and treated in lots of 2 grams with 16 grams (1 mol.) of acetyl chloride mixed with its own volume of benzene, shaking well between each addition.

The mixture, which grows warm, should be heated for three hours on the water-bath to complete the reaction. The precipitated acetamide hydrochloride, which is practically insoluble in benzene, is collected, and the filtrate containing the diacetamide, which is readily soluble, is distilled to remove the benzene, and the residue fractionated. Some acetic acid comes over at first, and afterwards diacetamide, which distils at 215—220°, the liquid quickly solidifying to a crystalline, stellate mass on cooling. On recrystallisation from a mixture of benzene and light petroleum, it separates as fine needles melting at 78°.

0·3240 gave 39·5 c.c. moist nitrogen at 17° and 760 mm. N = 14·15.
0·1018 „ 12·2 c.c. „ 16° „ 748 „ N = 13·74.
$C_4H_7O_2N$ requires N = 13·86 per cent.

The yield is only 30—40 per cent. of the theoretical, but the method is an easy and convenient one. Acetamide may be readily recovered from the hydrochloride and used again.

The interaction of other amides and acid chlorides was also examined. No action occurs between acetyl chloride and benzamide, or between benzoyl chloride and benzamide. This, no doubt, is accounted for by the less basic nature of the latter; acetamide, on the other hand, immediately combines with the hydrogen chloride formed, and, disturbing the equilibrium in this way, admits of a change taking place in the direction of the above equation.

The action of benzoyl chloride on acetamide has been investigated by Pinner (*Ber.*, 1892, **25**, 1435), who found that it could be mainly represented by the equation:

$$CH_3{\cdot}CO{\cdot}NH_2 + C_6H_5{\cdot}COCl = CH_3{\cdot}CN + C_6H_5{\cdot}CO_2H + HCl.$$

On repeating this experiment, I have found that this does not express entirely what takes place. On treating the product after the reaction with cold dilute sodium hydroxide to remove the benzoic acid, an oil remains which solidifies on standing. On recrystallisation from alcohol and chloroform, it separated in long, flat needles melting at 42°, and was identical with benzoic anhydride (compare the action of benzoyl chloride on sodium acetamide, this vol., p. 396). The reaction, therefore, is partly expressed by a second equation:

$$CH_3{\cdot}CO{\cdot}NH_2 + 2C_6H_5{\cdot}COCl = CH_3{\cdot}CN + (C_6H_5{\cdot}CO)_2O + 2HCl.$$

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XLIII.—*Note on Two Molecular Compounds of Acetamide.*

By Arthur Walsh Titherley, M.Sc., Ph.D.

During the course of some experiments described in the foregoing paper (this vol., p. 411) upon the action of ethylene dibromide on sodium acetamide in presence of alcohol, a peculiar crystalline compound was isolated from the alcoholic solution after the reaction was over. The sodium bromide which separates during the change was filtered off, and the filtrate cooled or evaporated in a vacuum. In this way, long, colourless needles separated, which were at first mistaken for a condensation product of some kind, but always appeared to contain sodium bromide as impurity. Repeated crystallisation from alcohol, however, showed that the inorganic salt was not removed, and was an essential constituent. On investigation, the substance proved to be simply a well-defined molecular compound of the composition $2CH_3{\cdot}CO{\cdot}NH_2,NaBr$.

Similar experiments with alkyl iodides resulted in the formation of the corresponding, but much more soluble, compound, $2CH_3{\cdot}CO{\cdot}NH_2,NaI$.

These products are thus analogues of acetamide hydrochloride, $2CH_3{\cdot}CO{\cdot}NH_2,HCl$, and as no previous account of them appears to have been given, they were examined more closely. Both may be readily obtained directly from their constituents.

Acetamide Sodium Bromide, $2CH_3{\cdot}CO{\cdot}NH_2,NaBr$.—Powdered sodium bromide (1 mol.) and acetamide (2 mols.) are together boiled in five times their weight of absolute alcohol for about 3 hours. The bromide gradually dissolves, but not completely. On filtering hot and allowing to evaporate in a vacuum, or, better, by adding benzene, beautiful, long, white, glistening needles separate in feathery growths. The crystals, which are very deliquescent, may be dried in a vacuum, but not by heating, which causes dissociation, and they may be recrystallised from alcohol. When pure, it melts at 144—145° with separation of sodium bromide. On titration with $N/10$ $AgNO_3$:

0·3792 gave 0·1754 NaBr. NaBr = 46·2.

$2CH_3{\cdot}CO{\cdot}NH_2,NaBr$ requires NaBr = 46·6 per cent.

It begins to dissociate even at 100°, giving a crystalline sublimate of exceptionally pure acetamide (m. p. 83°), sodium bromide remaining. When dissolved in water, treated with chloroplatinic acid, and allowed to stand in the cold, the acetamide suffers gradual hydrolysis, and beautiful, large, ruby-red octahedra separate, consisting of an isomorphous mixture of $(NH_4)_2PtBr_6$ and $(NH_4)_2PtCl_6$.

Acetamide Sodium Iodide, $2CH_3{\cdot}CO{\cdot}NH_2,NaI$, is formed similarly to the above. Sodium iodide (anhydrous) dissolves more readily and completely than the bromide in an alcoholic solution of acetamide. The double compound is very soluble, and therefore the minimum quantity of alcohol should be used. On allowing the syrupy solution to stand in a vacuum, it crystallises out in beautiful, large, flat prisms, which are excessively deliquescent. It melts at about 110°, with separation of sodium iodide. On titration with $AgNO_3$:

0·1942 gave 0·01088 NaI. NaI = 56·00.

$2CH_3{\cdot}CO{\cdot}NH_2,NaI$ requires NaI = 55·98 per cent.

Attempts were made to prepare similar compounds with sodium chloride and with potassium haloids, but without success.

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XLIV.—*A New Method for the Measurement of Ionic Velocities in Aqueous Solution.*

By B. D. STEELE, B.Sc., 1851 Exhibition Scholar (Melbourne).

THE history of the investigation of the migration of the ions during electrolysis begins with the classical researches of Hittorf (*Pogg. Ann.*, 1853, **89**, 177; 1856, **98**, 1; 1858, **103**, 1; 1859, **106**, 337, 513; Ostwald's *Klassiker*, Nos. 21 and 23) who, by the measurement of the changes of concentration which take place during electrolysis in the neighourhood of the electrodes, measured the value of the ratio u/v, where u and v are respectively the velocities of the anion and of the cation. The ratio $u/u+v$ is called by Hittorf the transport number (*Ueberführungzahl*), and represents the ratio of the velocity of the anion to the sum of the velocities of anion and cation, or of the amount of current carried by the anion to the total current.

Kohlrausch, in his determination of the conductivity of salt solutions, has measured the constant $(U+V)$ the sum of the velocities of the anion and cation, which approaches a constant value in very dilute solutions, so that he is able to assign to certain ions values for u and v which are known as the specific ionic velocities.

In any particular solution of a salt, the average velocity is dependent on the driving force or fall of potential, on the specific velocity, and on the coefficient of ionisation, or $(U+V)=\pi\, x(u+v)$, where U and V are the average velocities, and u and v the specific velocities, so that for a potential slope of 1 volt per cm. $U=xu$ and $V=xv$.

The first direct measurement of U or the mean velocity of the ions

was made by Lodge (*B.A. Report*, 1886, 395), who observed the progress of a margin which moved through a gelatin solution, and thus marked the advance of the ion whose velocity he wished to determine. Since the observed velocity is conditioned by the fall of potential π, it is necessary that the latter should be regular, and that it should be known before U can be determined. These conditions were not fulfilled in the experiments of Lodge, who assumed that in a tube which was 40 cm. long and with a difference of potential of 40 volts between the ends, the potential fall was 1 volt per cm. From the fact that the contents of the tube, originally homogeneous, became heterogeneous as a consequence of the passage of the boundaries, this could not possibly be the case. That the fall was not very irregular was shown, however, by the fact that his values for the hydrogen ion compare very favourably with those calculated by Kohlrausch.

Others of Lodge's experiments, as has been pointed out by Masson (*Phil. Trans.*, 1899, **192**, A, 331) were wrongly interpreted by him; thus, the velocities of the anion and cation boundaries were considered to indicate the comparative velocities of the following ion in each case, as, for example, in the experiments in which the velocity of Sr and Ba were compared with those of Cl, Br, and I, whereas the ratio of the velocity of the two boundaries is, in reality, conditioned only by the velocities of the ions of the intermediate salt, provided no mixing takes place at the boundary.

The conditions under which, in a series of two electrolytes having a common ion, a sharp boundary may be expected without mixing taking place during electrolysis, are pointed out for a special case by Whetham (*Phil. Trans.*, 1893, A, 337), and for the more general case by Kohlrausch (*Ann. Phys. Chem.*, 1897, [iii], **62**, 209). In the latter paper, the deduction is drawn that a boundary may be obtained in any system where there is a change in transport number, in the sense that the following ion has a slower specific velocity than the preceding one, a conclusion supported shortly afterwards by Weber (*Sitzungsb. Akad. Wiss. Berlin*, 1897, 936).* Kohlrausch further states that with two ions of different velocities, and a boundary between, the velocity of the boundary is intermediate between those of the two ions, each boundary, in reality, marking the velocity of two ions, that of the preceding faster ion under one driving force (fall of potential), and that of the following slower one under a different and greater driving force.

Masson (*loc. cit.*) has shown experimentally that the relative velocity of the boundary at each end of a homogeneous solution is conditioned only

* In a paper in which the theory and practice of the determination of Hittorf's transport numbers are fully discussed, Bein (*Zeit. physikal. Chem.*, 1898, **27**, 1) sets forth very clearly the general conclusions arrived at by Kohlrausch and Weber in the papers mentioned.

by the nature of the preceding ion in each case, and that the relative velocities of two such margins are the same whether Cu and CrO_4 or Cu and $C_4H_4O_6$ ions follow; he also gives experimental proof of the fact that if the faster ion follows the slower, mixing takes place and the preceding statement no longer holds.

The author has found that even in this case it is possible to obtain a clearly marked boundary, but it no longer moves with a constant velocity, in other words, the ratio of the velocities of the boundaries at each end of a homogeneous solution is no longer constant when one of the following ions travels faster than the one in front of it.

The method described by Masson for the measurement of ionic velocities compares directly the velocities of the boundaries at the anode and cathode end of a gelatin solution of the salt under investigation. The position of the margin is marked by the difference in colour of the measured and the indicator ions, thus, in the experiment with potassium chloride, the margin at the anode end was between Cu and K, that at the cathode end between CrO_4 and Cl, the potential slope π in the equation $U+V=\pi\ x(u+v)$, conditioning the velocity was unknown; the average working velocities U and V only being measured. The values of $x\ u$ and $x\ v$, the absolute velocities for the particular concentration, could not be calculated.

That π, although unknown, was the same for the anion as for the cation follows from the homogeneous nature of the conducting medium between the boundaries, and from the fact that the tube was carefully calibrated and of even cross section.

In the experiments hitherto described, the influence of the gelatin is quite unknown, the assumption being made that all ions would be influenced to the same extent, if at all.

Whetham (*loc. cit.*), avoiding the use of gelatin, measured the velocity of the moving boundary in aqueous solution. A single boundary only, that between two salt solutions having a common ion, was observed, and absolute, not comparative, measurements were made. Any uncertainty as to the regularity of the fall of potential was removed by the selection of such pairs of solutions as had equal or nearly equal specific conductivities. A vertical tube was employed, and the margin observed was that between a coloured and a colourless solution; the results obtained were in close accordance with those calculated for the same concentration from Kohlrausch's conductivity measurements.

This method is, however, very limited in its scope, on account of the difficulty of finding pairs of solutions that fulfil all the necessary conditions; it is further limited, in common with Masson's method, by the necessity for the employment of coloured indicator solutions, as it is not possible to find a suitable coloured anion indicator

which will not give a precipitate with, for example, the alkaline earth and the heavy metals.

New Method of Measuring Ionic Velocities.

This method is in principle the same as Masson's inasmuch as the velocity of movement of a margin between two solutions is measured, the measured ion being followed in all cases by an indicator ion of specifically slower velocity. Like Masson's, also, it is a method of comparison; in a given experiment the velocities of the boundaries at the anode and cathode end of a homogeneous solution are compared, both being driven by the same, unknown, potential fall per centimetre.

The method differs, however, from Masson's in two essential respects, firstly, the measurements are made in water and not in gelatin, and secondly, the employment of a coloured ion as indicator is not necessary, all that is required being that a solution of the indicator containing about the same number of gram-molecules per litre as the measured salt solution should differ from the latter in density and in refractive power. The choice of indicators is thus very largely increased. The method fails to determine accurately xu and xv, since it has not as yet been found possible to measure π directly, although this may be calculated very approximately.

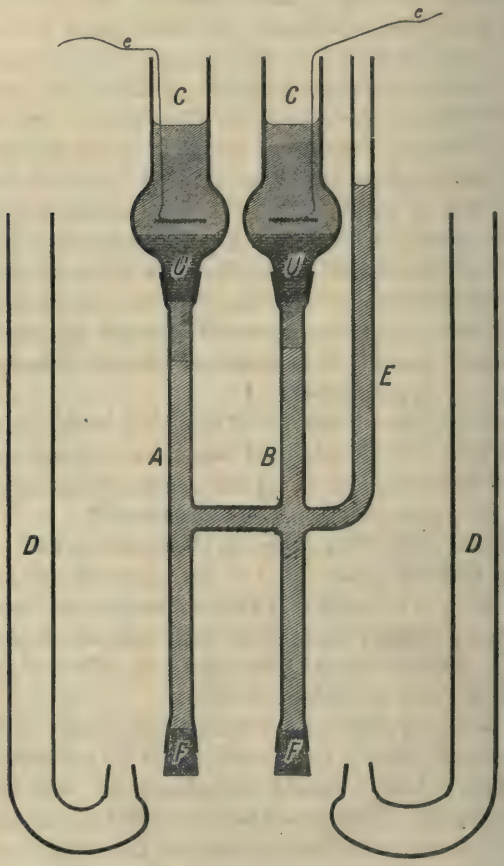
The essential feature of the method consists in the imprisonment of the aqueous solution to be measured between two partitions of gelatin containing the indicator ions in solution, thus preventing displacement of the liquid during the course of an experiment.*

The apparatus employed is shown in the figure (p. 418). *A* and *B* are two carefully selected glass tubes of the same area of cross section; these are joined by a short tube of larger diameter, and each can be connected at either end by means of well ground and well fitting stoppers with another vessel *C*, *C*, and *D*, *D*. Two of these vessels are used with the tube in each experiment.

Since it is necessary that there should be no mixing of the solutions by gravity currents during an experiment, it is necessary that in all cases the heavier solutions should be underneath. For an experiment in which the indicator solutions are heavier than the measured solutions, the vessels *D* are employed, and in this case the margins are measured as they travel from below upwards; when both indicator solutions are lighter than the salt solution, the vessels *C* are used, and the boundary travels from above downwards; finally, when one indicator is lighter, and the other heavier, than the salt solution, one of the vessels *C* and one of *D* are employed.

* An attempt has been made to substitute a porous earthenware membrane for the gelatin, but without success, as it was found that the liquid was forced through the membrane in the direction of the anode.

The vessels to be used in an experiment (in the figure, C, C) are first filled with a gelatin solution of the indicator, the depth of gelatin being about 2·5 cm. The strength of the gelatin solution is such that it is not of less molecular concentration than the salt solution. It has been found necessary that the portion of the apparatus containing the jelly should be of larger sectional area than the tube; when this is not the case, the heating by the current, being greater in this portion



of the tube where the resistance is greater may result in the melting of the jelly. For this reason, the ends of the tubes are enlarged in the manner shown in the diagram. It is essential, however, that this enlargement should be as shallow as possible, since, if the volume is too great, it is found that no margin is produced. In an experiment the tubes A and B are first filled with the solution to be examined, one end of each tube being closed with a rubber stopper, F, the cathode and anode cells

are placed in position, care being taken not to enclose any air bubbles. The tube *B* is also fitted with a side tube *E* so that the liquid may be free to expand or contract. The current is started by pouring into the vessels an aqueous solution of the same indicator as that contained in the jelly, the cathode and anode being previously placed in position, and the whole operation is carried out as rapidly as possible, to avoid mixing by diffusion at the boundary between jelly and solution. The apparatus is then completely immersed in a specially constructed water-bath, which consists of a metal vessel two parallel sides of which are fitted with large plate glass windows.

The current employed was obtained from a battery of 30 lead accumulators, and the voltage used varied in the different experiments. The measurement of the current in some of the earlier experiments was made by means of a copper voltameter, but it was found that the quantities of electricity involved were too small to allow of accurate measurements by this method. For the subsequent experiments, a sensitive galvanometer was therefore substituted, whose readings were certainly accurate to less than 1 per cent.

The Margin between Indicator and Solution.

At the beginning of an experiment, the boundary between indicator and solution is coincident with that between the gelatin and aqueous solutions; after the lapse of a short time, which varies with the nature of the salt and with the potential slope, the margin has advanced in both tubes from the gelatin, as shown in the figure, where the darker shaded portion represents the indicator, and *U* represents the gelatin partitions, so that now there exists an aqueous system :—

Anion indicator | salt solution | cation indicator

which contains the two boundaries under observation. From this time onwards, the presence of the gelatin can have no influence on the ionic velocities, which are conditioned only by the potential slope, and by the nature of the salt in solution. It has been already mentioned that in order to see the boundary, it is not necessary to have a coloured ion as indicator ; when the boundary is looked at by transmitted light, it is seen with great distinctness, on account of the difference in refraction of the two solutions. Even in solutions which differ in density so slightly as do half-normal solutions of potassium chloride and potassium acetate * (the difference in density is in the fourth decimal place), the margin is distinctly to be seen, although it can no longer be distinguished with more dilute solutions of these two salts. A margin is, however, still

* As pointed out by Masson, the concentration of the indicator solution is not the same as that of the solution it follows, but is in all cases somewhat less ; no error, however, is introduced by neglecting, for the present, this change in concentration.

distinctly visible with decinormal potassium bromide, using potassium acetate as indicator. The fact that, owing to a difference in the refraction, a boundary may be observed between colourless solutions, has been previously noted by Lenz (*Mem. Akad. St. Petersburg*, 1882, [vii], 30, No. 9, 86), who observed such a boundary between solutions of cadmium chloride and sodium chloride, and the same phenomenon for the same pair of solutions was also noticed by Bein (*loc. cit.*). It may be mentioned that this boundary between cadmium and sodium is much more distinctly to be seen than any other; but as will be explained immediately, it is (in aqueous solution) by no means one at which no mixing takes place, nor can it be used for the observation of any ionic velocity.

The movement of the margin is measured by means of a cathetometer, and to ensure accuracy in the readings, the water-bath is provided, as already stated, with windows of plate glass, to obviate errors in reading due to uneven refraction at the surface. A small gas jet is placed behind each tube, and this, when viewed through the telescope of the cathetometer, is seen to be cut by a dark line at the boundary between the two solutions. Each tube has a horizontal line etched on it which serves as a fixed point from which the measurements are made, so that any slight displacement of the apparatus during an experiment does not vitiate them.

The method of measuring is as follows. After the margins are well within the tubes *A* and *B*, their distances from the fixed mark are measured, the time at which the measurements are made also being noted. At intervals of about 10, 15, or 20 minutes, the distance between the margin and the fixed mark is again measured, the difference between the first and subsequent readings giving the distance the margin has moved in the given time. From the second, third, and succeeding readings, values for u/v or $u/(u+v)$ are obtained, the average from all these readings being taken. The actual figures obtained in an experiment with, for example, *N*-potassium bromide will make this clear.

Cation margin.			Anion margin.			$\frac{d'}{d}=\frac{u}{v}$.	$\frac{d'}{d+d'}=\frac{u}{u+v}$
Minutes.	*D*.	*d*.	Minutes.	*D'*.	*d'*.		
0	78·6	—	0	65·3	—	—	—
30	65·4	13·2	30	53·0	12·3	0·930	0·482
54	55·8	22·8	54	44·9	20·4	0·895	0·472
72	49·6	29·0	72	39·1	26·2	0·903	0·474
103	38·6	39·9	103	29·8	35·5	0·893	0·472

Columns *D* and *D'* give the distances in mm. between the boundary and the fixed mark, for the cation and the anion respectively; *d* and *d'* give the distances in mm. moved over by the two boundaries.

The distances considered are always measured from the first reading, so that in the earlier numbers the percentage error due to the reading of the cathetometer is much greater than in the later ones. On this account, in taking the average, each value for $u/(u+v)$ is multiplied by the distance in millimetres through which the boundary has passed at the time the observation was made; the numbers so obtained are added together and their sum is divided by the sum of the multiplicands. In most of the experiments, this made little or no difference in the result, but in one or two, where there was perhaps a greater error in the first readings, it was of more consequence.

Masson has pointed out four conditions which must be fulfilled by the indicator ions in order that a sharp margin, moving with uniform velocity may result. These are as follows:

(1) The indicator ions must have a strong and characteristic colour.

(2) The ions must not be such as to react chemically on the solutions to be examined.

(3) During electrolysis, the cell solutions must not give rise to other species of ions which would move faster than and overtake the measured ion, thus altering the potential slope within one or both boundaries.

(4) The indicator ions must have a specific velocity slower than that of the ion to be measured.

These conditions apply to the measurement in gelatin. In aqueous solution, in addition to the last three, which must also be fulfilled, certain other conditions are necessary for the production of a boundary which moves with constant velocity; but even when Masson's fourth condition is not fulfilled, a boundary may be seen, although it cannot be taken as marking the position and hence the velocity of the ions of the intermediate solution.

A point of much importance is the relation between the resistances of the two electrolytes. It is necessary in all cases to select as indicator a solution of a salt which has a resistance not very much greater than that of the solution to be measured; thus it has been found that for experiments with magnesium sulphate a very good margin between the cations is obtained with cadmium sulphate or copper sulphate as indicator, and one which maintains a constant ratio with the corresponding anion margin throughout an experiment. Neither of these salts, however, can be used as an indicator for potassium salts, as is evident from the following results, which are expressed in terms of the Hittorf transport number. The value of $u/(u+v)$ for potassium chloride found by Hittorf was 0·515, that determined by this method with cadmium sulphate or copper sulphate as indicator varied in four experiments from 0·9 to 8·0: numbers which are

obviously incorrect. But with lithium chloride as indicator a constant value is obtained, constant not only throughout one experiment, but through a series of six experiments. The cause of the irregular results found with cadmium or copper as indicator has been traced to the heating effect of the current. From Ohm's and Joule's law, $H = EC = C^2R$, it is seen that throughout any circuit where C is constant, the heating effect is proportional to the resistance and therefore the distribution of the heating in the circuit is also proportional to R; if, therefore, there exists in the circuit a short column of liquid of much greater resistance than the rest of the circuit, the heat is concentrated in this column and currents are set up in the liquid with the result that mixing takes place. That this is the case may be seen on examining carefully the boundary between such a pair of electrolytes as copper sulphate and potassium sulphate; the margin is observed to be sharp and very distinct, but not perfectly horizontal, being instead wavy, as if subjected to some disturbing influence, but presently a thin stream of coloured liquid is seen to rise from the copper sulphate solution and mix with the overlying potassium sulphate solution, and after about an hour the whole column of liquid between the two jellies has become blue. In one experiment, the mixing that took place was so great that the margin, after advancing for about half-an-hour, actually began to move backwards.

With all the salts examined this difficulty has been overcome by the selection of an indicator which has not a very much greater resistance than the salt to be examined. In all cases, the resistance is much diminished if the indicator is placed above the solution (when this is possible), since, as the resistance is greater in the indicator, the heating effect is greater also, consequently the upper solution tends to become still lighter and the danger of mixture with the lower solution to become less.

The influence of the voltage on the production and maintenance of a good margin is very considerable, and it would seem from the experiments, more or less of a preliminary nature, which have been carried out that for each pair of solutions forming an electrolytic boundary of the kind under discussion, there is a certain range of potential fall which is capable of producing a boundary of sufficient sharpness for observation without the production of too great a current density and consequent heating effect. This range is apparently much greater for some pairs of ions than for others.

Without at present offering any explanation, the following facts may be mentioned. With the apparatus employed, a difference of voltage between the electrodes of 20 volts corresponds to an average potential fall of about 1 volt per cm.

(1) With a normal solution of sodium bromide, and using lithium

chloride and sodium acetate as indicators, with a potential fall between the electrodes of 20 volts, values for $u/(u+v)$ were found varying between 0·597 and 0·572, showing that some disturbing influence was at work. With a voltage of 24 and 27 volts, in separate experiments, much less constant results were obtained, and the margin in all cases had the appearance of being washed away, being wavy and not horizontal.

(2) With decinormal sodium bromide solution, results were obtained varying in different experiments from $u/(u+v) = 0{\cdot}50$ to $0{\cdot}55$, and here the influence of the voltage was very marked, for with a total voltage between the electrodes of 26 volts, no margin could be detected between lithium bromide and sodium bromide, although a distinct one was present at the cathode end, whilst with 30 volts a margin between the solutions was obtained which was exceedingly wavy and not horizontal and showed obvious signs of being washed away.

(3) With magnesium sulphate, using sodium acetate as anion indicator, four experiments were carried out. With a fall of potential of 24 and 26 volts, no boundary could be detected; with 30 volts, the boundary could be located, but could not be read with any degree of accuracy, being very indistinct, and, as it seemed, spread out; with 34 volts, a clearly defined margin was produced, which could be read with certainty. On reducing the voltage to 30, the margin became indistinct, whilst on again increasing it to 34, the boundary once more became clear and distinct, but not so good as at first.

(4) As previously mentioned, with Mg followed by Cd ions, a very good and constant margin is produced, the voltage being 40, whilst with potassium sulphate and cadmium sulphate a potential fall of 20 volts was too great, giving a very sharp and clear-cut margin, but one which was very irregular in its rate of motion, and gave every indication of being washed away.

In this connection, it is worthy of mention that in preliminary experiments it has been noticed frequently that if the current is shut off for one or two minutes, the boundary disappears, and can no longer be read by the cathetometer, but that on again closing the circuit, the boundary reappears after about ten minutes, but never with such clearness as in an undisturbed experiment. The possibility of a boundary being formed in this manner during electrolysis is demonstrated by Kohlrausch in the paper previously cited.

It has been found necessary to employ tubes of different sizes for different salts, and different concentrations of the same salt. Within certain limits, the size of the tube has no influence on the constancy of the results, but with good conductors the amount of current is too great in a large tube, and the correspondingly greater heating effect has a disturbing influence.

Two sizes of tubes have been employed; the larger, used for more dilute solutions, has an area of 0·3965 sq. cm. in cross section, and the smaller, used for the stronger solutions, has a sectional area of 0·1213 sq. cm.

The gelatin employed was the best commercial gelatin, which had been purified by diffusion in distilled water, in the manner described by Lobry de Bruyn (*Rec. Trav. Chim.*, 1900, **19**, 236).

The gelatin solutions of the indicator contained 12 per cent. of gelatin, except in the case of the twice normal lithium chloride jelly, which contained 20 per cent. of gelatin, as a 12 per cent. jelly would not set in this case.

The indicator solutions were always of such a strength that they were a little stronger in equivalents than the measured solution. Five indicators have been employed.

Cation indicators:

Copper sulphate with copper anode, to minimise as far as possible the formation of hydrogen ions.

Cadmium sulphate, using a cadmium anode.

Lithium chloride with lithium carbonate suspended in the solution, to prevent hydrogen ions finding their way into the jelly.

Anion indicators:

Sodium acetate with a small proportion of acetic acid to prevent the formation of OH ions.

Potassium chromate with potassium dichromate, also to prevent the formation of OH ions.

Experimental Results.

TABLE I.

Salt.	N.	Indicators.	$u/(u+v)$.			
			a.	*b.*	*c.*	*d.*
$MgSO_4$	2	$CuSO_4$ and K_2CrO_4	0·729	0·732	0·750	0·693
	2	$CuSO_4$,, $NaC_2H_3O_2$	0·734			(0·688)
	2	$CdSO_4$,, $NaC_2H_3O_2$	0·738	0·744		
	2	LiCl ,, $NaC_2H_3O_2$	0·56 to 0·61			
$CdSO_4$	2	LiCl ,, $NaC_2H_3O_2$	0·62 to 0·65			

Table I shows that the ratio of the velocities u/v or $u/(u+v)$ is independent of the nature of the indicator employed, provided it has a specifically slower velocity than the preceding ion.

This condition is fulfilled by the anion in all the experiments cited and by the cation in the first three, and for these a number differing only slightly from 0·734 is obtained, whatever indicator is employed (further, the ratio throughout any experiment does not differ to any appreciable extent from the mean, and different readings show an irregular divergence on both sides of the mean).

The fourth and fifth experiments correspond to the case where the required conditions are not fulfilled, the velocity of the indicator being greater than that of the preceding Mg or Cd ion. In these experiments, the boundary was very much less distinct than in the others, but was quite decided enough to be read with certainty, but corresponding to the mixing that takes place at one of the boundaries is a change in the potential fall for that part of the tube, and a consequent change in the ratio of the measured velocities. For comparison with these numbers, the value for $u/(u+v)$ was determined by Hittorf's method, and the results of the two experiments carried out are given in column *b*. In column *c* is given the value for the transport number recorded by Kohlrausch and Holborn (*Leitvermögen der Electrolyte*). In column *d* is given the value 0·693 found by Masson by direct measurement of the velocity of the margin in gelatin, and underneath this in brackets the figures 0·688 refer to the value found by the author, who, for purposes of comparison, has repeated this experiment in gelatin.

It thus seems that the ratio of the velocities of the Mg and SO_4 ions in magnesium sulphate are considerably influenced by the presence of gelatin in solution.

In table II (p. 426) are given the results obtained for different concentrations of salts of the type of sodium chloride.

The first column indicates the salt; the second column under N gives the number of gram-molecules (gram equivalents) per litre; and the next four columns give the values for $u/(u+v)$ obtained by the different methods. Column *a* shows the number obtained by direct measurement in aqueous solution. In the majority of instances, the figures given are the average from a single experiment, but for the first salts measured a number of experiments were made, thus for $2N$ potassium chloride six experiments were carried out, the mean number obtained in each being respectively 0·492, 0·490, 0·494, 0·488, 0·488, 0·489; similarly for N potassium bromide, two experiments gave 0·473 and 0·4735. As an example of the degree of accuracy which may be obtained in single readings of the velocity of the margin, the figures obtained in two experiments may be quoted.

The figures agreeing most closely were obtained with $N/2$ potassium bromide solution; the successive measurements gave 0·477, 0·480, 0·480, 0·477, 0·476.

TABLE II.—*Indicators: lithium chloride and sodium acetate.*

Salt.	N.	$u/(u+v)$.					c/c^1.
		a.	*a'*.	*b*.	*c*.	*d*.	
KCl	2·0	0·489	0·493—0·486	0·483	0·503	—	1·009
	1·94	—	—	—		0·516	
	1·0	0·488	0·493—0·486	0·490		—	—
	0·7	—	—	—		0·515	
	0·5	0·490	0·491—0·488	0·495		—	0·984
NaCl	2·9	—	—	—	—	0·647	
	2·0	0·590	0·595—0·587	0·587	0·600	—	1·004
	1·0	0·592	0·593—0·587	0·595		—	0·989
	0·8	—	—	—		0·634	—
	0·5	0·597	0·603—0·596	0·598		—	—
KBr	3·1	—	—	—		0·528	
	2·0	0·468	0·472—0·462	—		—	0·998
	1·0	0·473	0·477—0·470 0·482—0·472	—		—	1·031
	0·5	0·478	0·480—0·476	—		—	1·004
	0·1	0·483	0·486—0·479	—		—	0·978
	0·07	—	—	—		0·514	
NaBr	0·5	0·595	0·597 –0·594	—		—	1·001

The numbers which show the least agreement are those for the $2N$ potassium bromide solution, namely, 0·472, 0·471, 0·471, 0·462, 0·466, 0·467.

In column *a'* are shown the extreme numbers obtained in each experiment, and in column *b* are the figures obtained by Masson for the same concentrations of the same salt measured in gelatin. A comparison of the figures in *a* and *b* shows a very close agreement between them, and affords no such evidence of a disturbing influence of the gelatin as is seen with the figures for the magnesium sulphate solution (Table I). Apparently certain ions are very much more influenced by the presence of gelatin than others.

Column *c* gives the latest values calculated for infinite dilution by Kohlrausch (Kohlrausch and Maltby, *Wiss. Abhandl. Physik. Tech. Reichsanstalt*, 1900, **3**, 157), and column *d* gives the numbers obtained by Hittorf for the concentrations nearest those measured. The last column gives under c/c' the ratio of the current measured by the galvanometer to that calculated from the observed velocities $(U+V)$ according to the equation:

$$C = An\,(U+V)\eta \text{ where}$$

η = the electrochemical equivalent of hydrogen.
A = the area of cross section of the tube containing the solution.
n = the number of gram-equivalents per c.c.
$U + V$ = the sum of the observed velocities of the two ions.

The quantity $\frac{C\eta}{An(U+V)}$ should therefore be equal to unity.

It will be seen that the ratio in question shows as close an approximation to unity as can be expected. The ratio for the magnesium sulphate solution has not yet been determined, as in these experiments the current was not measured. For the N and $N/2$ potassium chloride solutions and the $N/2$ sodium chloride solution, the current, as already stated, was determined by a copper voltameter which, by direct comparison with an accurate galvanometer, was afterwards proved to give values much too low, and it is a well known fact that outside certain limits the copper voltameter is not capable of giving accurate results.

In the other experiments, the current was read every five minutes, and the readings plotted in a curve with the time in minutes as ordinate. The curve so obtained is not a straight line, but is slightly hollow, the current falling away more rapidly at first than afterwards, the average current for comparison with that calculated from the velocities was obtained from the area of the time-current curve.

It has been already pointed out that the method in the present form is a comparative one and does not directly determine the fall of potential by which the ions are driven; nevertheless, this fall of potential is capable of being calculated, for since electrolytes have been shown by Kohlrausch and others to obey Ohm's law, the relation

$$E = CR,$$

holds good for them. Now in an experiment the current is measured with considerable exactness. The resistance for a solution of a given concentration can be determined or is known from Kohlrausch's measurements. From a knowledge of the sectional area of the tube, the resistance per cm. can be easily calculated, and from this and the current the fall of voltage per cm. is obtained; so that it is possible to reduce the velocities recorded in Table II to absolute velocities which may be compared with Kohlrausch's values, as is done in Table III (p. 428).

In columns 1 and 2 the formulæ of the salts and the molecular concentration of the solutions are given. Column 3 shows the velocity of the cation in cm. per second calculated for a potential difference of one volt per cm. The fourth column gives the corresponding velocity for the anion, and in columns 5 and 6 are given under $U(k)$ and $V(k)$ the values for the cation and anion velocities calculated for the same concentrations from Kohlrausch's measurements of the conductivity,

TABLE III.

Salt.	N.	$U=xu$.	$V=xv$.	$U(k)$.	$V(k)$.
KCl	2·0	0·000483		0·000476	
	,,		0·000458		0·000501
	0·5	0·000553		0·000535	
	,,		0·000529		0·000561
NaCl	2·0	0·000274		0·000254	
	,,		0·000395		0·000441
	1·0	0·000318		0·000287	
	,,		0·000452		0·000509
KBr	2·0	0·000538		0·000475	
	,,		0·000471		0·000524
	1·0	0·000542		0·000507	
	,,		0·000484		0·000547
	0·5	0·000568		0·000525	
	,,		0·000516		0·000567
	0·1	0·000630		0·000577	
	,,		0·000599		0·000625

the results for the decinormal potassium bromide solution being obtained by extrapolation from the numbers for stronger solutions.

A comparison of the figures shows that, on the whole, the direct observation of the velocity gives numbers which confirm those previously calculated, especially when it is borne in mind that the potential fall, calculated in the manner described, is probably only approximately correct. Further, the considerable influence of temperature on the conductivity is not taken into account in the preparation of this table, since the temperature at which the experiments were made was not in all cases determined; in most of the experiments it was about 14°, whilst Kohlrausch's figures refer to a temperature of 18°.

As required by the dissociation theory, it will be seen that, in all the salts examined, the velocity $U=xu$ shows an increase with dilution and consequent increase of the coefficient of ionisation x. This is best seen in the figures for the potassium bromide solution, since for this salt the measurements extend over a greater range of concentration.

Attempts have been made to obtain more accurate values for the fall of potential by direct measurement during the experiment, and although no results of any value for this purpose have been obtained, it may be of interest to describe the method tried.

A narrow glass tube, which by careful measurements was found to

have the same cross section (external) for about 15 cm., was cut in the centre of the calibrated part; each of the tubes thus obtained had three fine holes drilled through the wall by means of a fine diamond, the first hole being about 1 cm. and the second and third holes respectively 2 and 4 cm. from the end of the tube. A platinum wire was then brought through each hole from the inside and the wires were insulated from each other by filling the tube with sealing wax, the protuding ends of the wires being finally cut off and filed smooth. One of these tubes was then placed in each of the tubes *A* and *B* through the rubber corks, *F*, *F*, so that in each tube there was a platinum point 1, 2, and 4 cm. from the gelatin, the wires from which were connected with apparatus by means of which the potential difference between each or any of the six points could be measured. At the beginning of an experiment the potential fall would be uniform and the same in each of the tubes *A* and *B*, since the external and internal tubes were both of even cross section.

It was found that the amount of polarisation between the points was too great and too variable in different parts of the system to yield results of any value.

The use of platinised points diminished the polarisation, but it was still much too great and too uneven. As a general result of these trials, however, it has been found that, as required by the theory, and in confirmation thereof, the fall of potential is in all cases much steeper in that portion of the system which contains the indicator solutions whose ions have a slower velocity than those which they follow.

It is intended to extend further the series of measurements, and in particular to investigate the application of the method to salts of a less simple type than sodium chloride.

In conclusion, the author desires to express his thanks to Professor Abegg for the help and encouragement he has received from him during the whole course of the work.

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XLV.—*Isomeric Salts containing Quinquevalent Nitrogen. Part VII. Benzylhydrindamine Bromocamphorsulphonates.*

By Frederic Stanley Kipping, Ph.D., D.Sc., F.R.S., and Harold Hall, A.I.C.

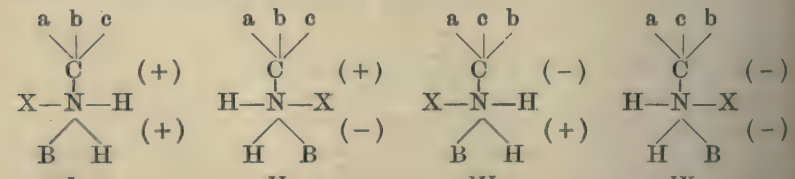
Benzylhydrindamine, a base prepared by treating *dl*-hydrindamine with benzyl chloride, combines with *a*-bromocamphorsulphonic acid, forming a salt which, on fractional crystallisation, is resolved into isomerides of the composition $C_{16}H_{17}N,C_{10}H_{14}BrO\cdot SO_3H$.

The more sparingly soluble *a*-compound differs from the more readily soluble *β*-compound in appearance, melting point, and other ordinary properties, and although the specific rotations are practically the same in alcoholic they become dissimilar in chloroform solution.

When the two isomerides are separately decomposed with barium hydroxide, they both give an optically inactive benzylhydrindamine, and the ammonium bromocamphorsulphonate obtained from the solution of the barium salt is, in both cases, identical in ordinary and in optical properties with ammonium *d*-bromocamphorsulphonate; consequently the two isomerides consist of the same base and the same acid.

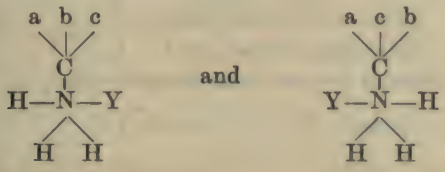
Judging by analogy, the isomerism of these two salts is of the same peculiar character as that of the hydrindamine bromo- and chloro-camphorsulphonates and *cis*-*π*-camphanates (Kipping, Trans., 1900, 77, 861), but whereas in the latter the nitrogen atom is united with only *three* different atoms or groups, the benzylhydrindamine salts contain a nitrogen atom directly combined with the radicles H, C_9H_9, C_7H_7, and $C_{10}H_{14}BrO\cdot SO_3$.

Now the presence of four different groups attached to nitrogen might determine the existence of enantiomorphously related optically active forms, and since benzylhydrindamine contains an asymmetric carbon group, if the arrangement of the groups around the nitrogen atom is really such as to give rise independently to further optical isomerism, the following four hydrochlorides of benzylhydrindamine would, theoretically, be capable of existence:



These four isomerides might therefore be expected to unite in pairs (I and IV, II and III) to form two externally compensated or racemic salts differing from one another in ordinary properties.

If, however, the chlorine atom, X, in the above compounds be displaced by the ion of *d*-bromocamphorsulphonic acid, the forms I and IV, II and III are no longer enantiomorphously related, and the formation of externally compensated salts is therefore impossible; on the other hand, two partially externally compensated salts might be formed, just as in the case of many of the salts of hydrindamine, and for the same reasons. Whether the observed isomerism of the benzylhydrindamine bromocamphorsulphonates should be attributed to the existence of four optically active ammonium bases, enantiomorphously related in pairs, as indicated by the above formulæ, or whether it should be considered to be analogous to that of the hydrindamine bromocamphorsulphonates, there is no means of deciding with certainty from the facts at disposal; there is, indeed, no considerable difference between the two views in question, except that in the case of the hydrindamine salts the enantiomorphous relationship of the forms



may be left open (*loc. cit.*, p. 869).

The fact that both salts afford an optically inactive benzylhydrindamine on decomposition is in accordance with either view, since when the base is liberated the nitrogen atom becomes tervalent.

The slight difference in the observed specific rotations of the salts in chloroform solution recalls the analogous observations made in the case of aqueous solutions of the hydrindamine compounds, but throws no light on their nature; if completely dissociated, they would probably both give the normal molecular rotation of the acid, but owing to their very slight solubility in water, their specific rotations in aqueous solution could not be determined.

For the same reason, namely, their slight solubility, it is not very easy to convert the isomerides into well-crystallised salts of some optically inactive acid. When, however, a solution of the β-salt is treated with a solution of picric acid, a precipitate of benzylhydrindamine picrate is obtained. This salt is identical in melting point and in crystalline character with the picrate obtained by precipitating a solution of benzylhydrindamine hydrochloride.

Now if the isomeric benzylhydrindamine bromocamphorsulphonates

represented salts derived from two different externally compensated bases, as formulated above, the β-salt might be expected to give a picrate different from that obtained from benzylhydrindamine hydrochloride, because whereas the latter would contain all four bases, the β-salt would contain only two of them, I and IV, or II and III; the fact, then, that the picrates are identical in outward properties, taken in conjunction with the apparent homogeneity of the hydrochloride of the base, seems to show that the original benzylhydrindamine has not been resolved into isomeric externally compensated bases, or, in other words, that the existence of its two bromocamphorsulphonates is not caused by *optical* isomerism of the groups united to nitrogen. The evidence, however, is not satisfactory, and the whole problem is of considerable complexity so, for the present at any rate, it seems preferable to regard the isomerism of the benzylhydrindamine salts as being analogous to that of the salts of hydrindamine.

Accepting the latter view, isomerism of this kind has now been observed in the case of the

Hydrindamine bromocamphorsulphonates (Trans., 1900, 77, 861)
„ chlorocamphorsulphonates („)
„ *cis*-π-camphanates, and („)
Benzylhydrindamine bromocamphorsulphonates.

The following compounds, however, namely:

Hydrindamine *d*-camphor-π-sulphonate (this vol., p. 370)
„ *d*-mandelate „
„ *d*-camphor-α-sulphonate (this paper)
„ *d*-hydroxy-*cis*-π-camphanate („)

do not afford any evidence of the existence of isomeric forms when they are fractionally crystallised.

It will be obvious from this summary that the nature of the isomerism in question is of a very peculiar character, inasmuch as with one and the same base, namely, *dl*-hydrindamine, acids which are very closely related to one another give different results: α-bromocamphorsulphonic acid gives separable isomerides differing very considerably in ordinary properties, whilst its simple reduction product, camphor-π-sulphonic acid, gives an apparently homogeneous salt; again, *cis*-π-camphanic acid affords separable isomerides somewhat similar to one another in properties, whereas its hydroxy-derivative gives a salt which is apparently homogeneous.

These remarkable facts, and the discovery that ordinary *d*-bromocamphorsulphonic acid contains a small quantity of the corresponding *l*-acid (this vol., p. 370), raised misgiving as to whether the formation of these isomeric salts might not after all be caused by the presence of

some isomeride in the acids used, but a reconsideration of the facts and further experimental evidence show such a view to be untenable.

As previously stated (Trans., 1900, 77, 861), the more readily soluble β-salt can be partially converted into the α-salt in the case of the three pairs of isomerides already described; this fact has since been confirmed in the case of the *cis*-π-camphanates. It has also been shown that *some* ammonium bromocamphorsulphonate, identical in ordinary and in optical properties with the salt prepared from the α-isomeride, can be obtained from the more readily soluble β-salt; the further experiment described below proves that the *whole* of the acid in the β-salt consists of ordinary *d*-bromocamphorsulphonic acid.

Again, the hydrindamine *cis*-π-camphanates have (sometimes) widely different specific rotations in alcoholic solution, but give practically identical values when they are dissolved in water; this fact, and the partial conversion of the β- into the α-salt on evaporating with the *dl*-base, seemed to prove beyond doubt that the acids of the two isomerides were identical; in the course of further experiments with these remarkable salts, additional evidence, perhaps not wholly unnecessary in view of the origin and nature of the acid, has been obtained that this conclusion is correct.

So far, then, the facts established during the study of the salts described in these papers tend to bear out the theoretical views which have already been tentatively put forward to explain these cases of isomerism. The results of the investigation of the hydrindamine mandelates have shown, moreover, that *three* salts, which are optically different, namely, *d*A*d*B, *d*A*l*B, and *l*A*l*B may form a mixture which is not resolved into appreciably different fractions on crystallisation; it is therefore by no means improbable that, as already suggested, the product of the combination of an optically active acid with an externally compensated base may be a mixture of *four* optically different forms, which sometimes unite in pairs to form separable partially externally compensated salts, but sometimes give separable salts of the enantiomorphously related bases; from experience gained in working with various externally compensated acids and bases, it would seem that what has hitherto been generally regarded as the normal behaviour, namely, a separation of the optical antipodes, is in reality a somewhat exceptional result, and that in the majority of cases the two compounds unite to form a mixture of *d*A*d*B and *d*A*l*B or of *d*A*d*B and *l*A*d*B, as the case may be, which crystallises unchanged at the ordinary temperature.

The recently observed fact that tetrahydro-β-naphthylamine readily undergoes partial racemisation when liberated from its salts (Pope and Harvey, this vol., p. 74) might perhaps be thought to have some bearing on the question of the isomerism of the hydrindamine salts

considering the relationship between the two bases; and it might even be inferred that the α- and β-isomerides actually represent salts of the enantiomorphously related hydrindamines, which then at once undergo racemisation when set free from the acid. This possibility, however, has already been considered * and rejected (Kipping, Trans., 1900, 77, 878, 909), and the further evidence arising from the study of the benzylhydrindamine salts seems to exclude the possibility of any separation of the enantiomorphously related bases having occurred.

Benzylhydrindamine.

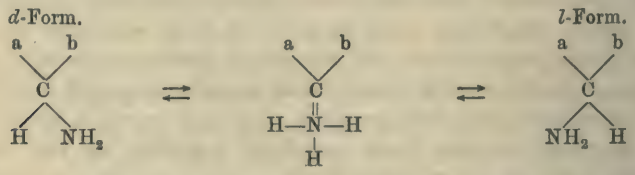
When benzyl chloride is added to an ethereal solution of hydrindamine, interaction occurs slowly at the ordinary temperature, crystals separate, and the change is completed by warming on the water-bath during some hours; after distilling off the ether and separating any unchanged benzyl chloride with a current of steam, the aqueous solution is evaporated to a small bulk, and the oily product which then separates is dissolved by the addition of a little alcohol; on cooling, benzylhydrindamine hydrochloride is deposited in almost colourless crystals and may be purified by recrystallisation from water or dilute alcohol.

For analysis, 0·2629 gram of a sample dried at 100° was dissolved in a large volume of boiling water, the solution acidified with dilute nitric acid and treated with silver nitrate: AgCl = 0·1394. Cl = 13·4.

$C_{16}H_{17}N,HCl$ requires Cl = 13·6 per cent.

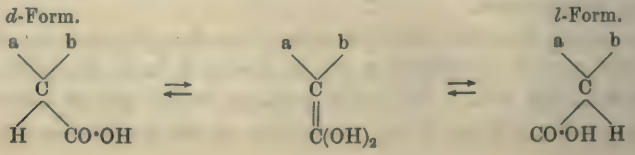
Benzylhydrindamine hydrochloride crystallises from water in very small prisms which melt at about 180—181° (corr.) when heated quickly,

* It was suggested that the mechanism of the change in such cases might be as follows.



This view has since been adopted by Pope and Harvey (*loc. cit.*), who apparently overlooked the fact that it had been previously advanced.

The readiness with which many substituted acids containing the asymmetric group in the α-position undergo racemisation may be accounted for in a similar manner:



but the melting point varies considerably with the experimental conditions and on continued heating even at about 175° the salt gradually liquefies; it is readily soluble in hot, but only sparingly so in cold water, and dissolves freely in cold alcohol.

The *base* is obtained as a colourless oil on treating a solution of the hydrochloride with an alkali; it is practically insoluble in cold water and has a neutral or only very feebly alkaline reaction to litmus; it volatilises in steam, but only slowly.

Benzylhydrindamine Bromocamphorsulphonates.

The base, liberated from the pure hydrochloride and separated by extracting with ether or distilling in steam, is treated with a slight excess of *d*-bromocamphorsulphonic acid in aqueous alcohol, and the solution evaporated if necessary; on cooling, crystals are deposited and by repeated fractional crystallisation of the first and subsequent deposits from boiling water or dilute methyl alcohol, two salts are obtained in a state of purity.

α-Salt.—The more sparingly soluble, or α-salt, separates from water in flat, thin, transparent plates melting sharply at 210—211° (corr.); it is almost insoluble in ether, and only very sparingly soluble in ethyl acetate or cold water, but dissolves comparatively easily in hot alcohol or cold chloroform. It is usually obtained in microscopic plates or fern-like masses, which, however, under the microscope, are easily distinguished from the crystals of the β-isomeride. The salt is anhydrous.

0·2 gave 0·0707 AgBr. Br = 15·0.

$C_{16}H_{17}N,C_{10}H_{14}BrO{\cdot}SO_3H$ requires Br = 14·9 per cent.

Determinations of the specific rotation of the α-salt gave the following results:

0·25 gram was dissolved in 96 per cent. ethyl alcohol, the solution diluted to 25 c.c. and examined in a 200 mm. tube: $\alpha_D = +1°0'$, whence $[\alpha]_D = +50°$ and $[M]_D = +267°$.

0·2 gram dissolved in chloroform, all other conditions as before, gave $\alpha_D = +40'$, whence $[\alpha]_D = +41·6°$.

0·4 gram dissolved in chloroform, all other conditions unchanged, gave $\alpha_D = +1°16'$, whence $[\alpha]_D = +39·7°$.

The base obtained from the α-salt is optically inactive: 1 gram of the salt decomposed with potash in the cold and the base extracted with ether gave an ethereal extract (about 20 c.c.) which showed no optical activity when examined in a 200 mm. tube.

In order to prove that the salt is derived from ordinary *d*-bromo camphorsulphonic acid, a sample was decomposed by warming it with a

solution of the calculated quantity of barium hydroxide; after cooling and extracting the base with ether (the extract was optically inactive), the aqueous solution of the barium salt was precipitated with ammonium carbonate, the filtered solution evaporated to dryness, and the residue heated on the water-bath until all ammonium carbonate had been expelled; the residual ammonium bromocamphorsulphonate was finally recrystallised from a very small quantity of water, dried, and its specific rotation determined in aqueous solution. The value obtained agreed with that of ammonium *d*-bromocamphorsulphonate.

β-Salt.—The more readily soluble, or β-salt, melts at 192—194° (corr.), and also differs from the α-isomeride in outward properties, being usually obtained in aggregates of poorly defined, microscopic prisms; it is anhydrous and its behaviour towards solvents is similar to that of the α-salt.

0·2 gave 0·0702 AgBr. Br = 14·9.

$C_{16}H_{17}N,C_{10}H_{14}BrO\cdot SO_3H$ requires Br = 14·9 per cent.

The specific rotation of this salt was determined in alcoholic and in chloroform solution:

0·25 gram was dissolved in 96 per cent. ethyl alcohol, the solution diluted to 25 c.c. and examined in a 200 mm. tube: $\alpha_D = +1°2'$, whence $[\alpha]_D = +51·5°$ and $[M]_D = +275°$.

Under the same conditions, but using chloroform as solvent:

0·2 gram gave $\alpha = +44'$: $[\alpha]_D = +45·8°$.
0·4 „ „ $\alpha = +1°22'$: $[\alpha]_D = +42·8°$.

It seems from these determinations that the isomerides have practically the same specific rotation in alcoholic solution, and that their molecular rotation in this solvent is the same as that of the fully dissociated salts of *d*-bromocamphorsulphonic acid; this might be a mere coincidence, but the experiments on the decomposition products of the isomerides show that the base of the salts is in both cases optically inactive, and that both salts contain *d*-bromocamphorsulphonic acid.

The specific rotation of the β-salt in chloroform solution seems to be rather higher than that of the α-isomeride, the above results having been obtained under exactly the same conditions in the two cases; the difference, however, is so small that it almost falls within the limits of experimental error, and in any case it is not of any great importance, as the values obtained for the specific rotation in such a solvent cannot throw any light on the nature of the salts.

That the base obtained from the β-salt is identical with that given by the α-isomeride was proved by decomposing the former with a

warm solution of the calculated quantity of barium hydroxide and then extracting with ether; the ethereal extract was optically inactive, and when shaken with hydrochloric acid it gave a benzylhydrindamine hydrochloride identical as regards melting point and outward properties with that obtained from the α-salt in a similar manner, and also with the hydrochloride of the original base. The solution of the barium bromocamphorsulphonate was precipitated with ammonium carbonate and the ammonium salt of the bromo-acid was purified as described in the case of the α-isomeride; the specific rotation of this ammonium salt was found to be identical, within the limits of experimental error, with that of ammonium *d*-bromocamphorsulphonate.

Benzylhydrindamine Picrate.

In order to obtain further evidence as to the nature of the base contained in the isomeric benzylhydrindamine salts, attempts were made to transfer the base directly from the bromocamphorsulphonic acid to some optically inactive acid; from an examination of the new salt, information might then be obtained as to whether the original base had or had not been resolved into different components.

Owing to the very slight solubility of the α-salt, which crystallises unchanged from moderately concentrated hydrochloric acid, the β-isomeride was employed, but even in this case the choice of methods is limited for a similar reason. Picric acid, however, precipitates the base from a solution of its bromocamphorsulphonate in very dilute methyl alcohol, in the form of a canary-yellow, somewhat sticky mass, which, on recrystallisation from aqueous methyl alcohol is deposited in slender, well-defined, transparent, yellow prisms or in more compact, poorly-defined crystals. This picrate, when heated slowly, sinters slightly at 159—160° and melts completely at 162—163°.

The picrate was also prepared from a sample of benzylhydrindamine hydrochloride in a similar manner and compared with that obtained from the β-salt; they melted simultaneously, appeared to be identical in crystalline character under the microscope, and, in short, no difference between them could be observed; a finely divided mixture of the salts from the two sources melted at the same temperature as its separate constituents.

dl-*Hydrindamine Camphor-α-sulphonate.*

The unsuccessful result of the attempts to isolate isomeric salts analogous to the hydrindamine bromocamphorsulphonates from the product of the combination of hydrindamine and camphor-π-sulphonic acid (Kipping, this vol., p. 370), led us to try and obtain such isomerides with the aid of Reychler's camphorsulphonic acid.

On neutralising this acid with an aqueous alcoholic solution of hydrindamine and then evaporating, the salt is deposited from the cold solution in long prisms or needles, but as it is very readily soluble in water it is most conveniently crystallised from a mixture of alcohol and ethyl acetate; by making use of these solvents and crystallising in a systematic manner, part of the product was finally obtained as two extreme fractions, which, however, proved to be identical in ordinary and in optical properties.

Hydrindamine camphor-α-sulphonate crystallises from water in transparent prisms melting at 167—168° (corr.) apparently without decomposing; it is very readily soluble in water, chloroform, or alcohol, less readily in ethyl acetate, and almost insoluble in ether; it separates in prisms from all solvents which were examined, and under the microscope no indication of the presence of different crystals is observed.

The salt is anhydrous, and a nitrogen estimation gave results agreeing with those required for the formula $C_9H_{11}N,C_{10}H_{15}O{\cdot}SO_3H$.

The specific rotation of the salt was determined in aqueous solution, the two extreme fractions being employed:

First fraction: 0·6 gram was dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube: $\alpha_D = +39'$, whence $[\alpha]_D = +13{\cdot}5°$ and $[M]_D = +49{\cdot}3°$.

Last fraction: 0·6 gram under the same conditions gave $\alpha_D = +38'$, whence $[\alpha]_D = +13{\cdot}2°$ and $[M]_D = +48{\cdot}2°$.

The molecular rotation of this camphorsulphonic acid has been determined by Pope (Trans., 1900, 77, 1085), who found it to be +51·7°; the above results accord fairly well with this value, and their close agreement with one another shows that no resolution of the salt has occurred, but whether it is a true partially racemic compound or a mere mixture, there is no evidence upon which to base a decision.

In alcoholic solution, the specific rotation is very much higher than in aqueous, as shown by the following determination:

0·5 gram dissolved in 96 per cent. ethyl alcohol, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave $\alpha_D = +1°2'$, whence $[\alpha]_D = +25{\cdot}8°$ and $[M]_D = +94°$.

This great difference between the values obtained in these two solvents is rather noteworthy when contrasted with the comparatively small difference caused by the substitution of alcohol for water in the case of *dl*-hydrindamine camphor-π-sulphonate.

dl-*Hydrindamine* d-*Hydroxy*-cis-*π*-*camphanate.*

The fact that *cis*-*π*-camphanic acid yields separable isomeric salts with *dl*-hydrindamine rendered it probable that hydroxy-*cis*-*π*-camphanic acid (Kipping, Trans., 1896, **69**, 947) would do so likewise, but experiment showed this inference to be unfounded.

On treating hydroxy-*cis*-*π*-camphanic acid with an aqueous solution of the base in slight excess and then concentrating, the salt is deposited in long, transparent prisms; by systematic crystallisation from dilute methyl alcohol, the original preparation was separated into two extreme fractions which, however, proved to be identical.

Hydrindamine hydroxy-*cis*-*π*-camphanate separates from dilute alcohol in prisms containing water of crystallisation.

0·5136 air-dried salt lost 0·0114 H_2O at 100°. $H_2O = 2·2$.

$C_9H_{11}N,C_{10}H_{14}O_5,\frac{1}{2}H_2O$ requires $H_2O = 2·5$ per cent.

The anhydrous compound melts at 206—207° (corr.), sintering a little at about 202°; it is readily soluble in cold alcohol or hot water, but the hydrated crystals are practically insoluble in chloroform, ether, or ethyl acetate. The specific rotation of the salt in aqueous solution was so low that it could not be determined with reasonable accuracy in dilute solutions, but a determination with a sample of the air-dried acid gave $[\alpha]_D = +10·8°$ in 2 per cent. aqueous solution; the identity of the two extreme fractions of the salt in melting point and in all ordinary properties may be taken as satisfactory proof that the base has not been resolved into its enantiomorphously related constituents.

Aqueous solutions of hydrindamine hydroxy-*cis*-*π*-camphanate soon become acid to litmus when they are boiled, the base escaping with the steam. It is possible that this fact, which no doubt indicates hydrolytic dissociation, is accountable for the failure to isolate isomeric forms of the salt, since, as already pointed out, the isomeric *cis*-*π*-camphanates, which also undergo hydrolytic dissociation to some extent, are partially converted one into the other in aqueous solution.

Hydrindamine Bromocamphorsulphonate.

The difficulty of explaining satisfactorily the formation of the two hydrindamine bromocamphorsulphonates, when considered in the light of the recent discovery of the existence of isomeric bromocamphorsulphonic acids (this vol., p. 370), seemed to render desirable some further experimental evidence in support of the view that the isomerides are derived entirely from the same acid and the same base.

As the *β*-salt is formed in such relatively small quantities, and as

this salt also gives a molecular rotation below the normal, it might be concluded that it contained a small proportion of the salt of *l*-bromocamphorsulphonic acid; such a conclusion, no doubt, would be difficult to reconcile with many of the facts already recorded, as, for example, the conversion of the β- into the α-isomeride on evaporating with the *dl*-base, and it is now shown to be quite untenable by the following experiment:

0·5 gram of a sample of the air-dried β-salt was dissolved in water, the solution diluted to 25 c.c. and examined in a 200 mm. tube; the average reading was $\alpha_D = +2°3'$, whence $[\alpha]_D = +51·25°$ and $[M]_D = +227·5°$, a result which agrees well with previous determinations.

The whole of the solution was then carefully washed into a flask, treated with $N/10$ sodium hydroxide solution in slight excess of the quantity required to liberate the base, and boiled until the latter was completely expelled; after cooling and diluting to 25 c.c. again, the solution, when re-examined in a 200 mm. tube, gave $\alpha_D = +2°22'$, whence $[\alpha]_D = +59·25°$ and $[M]_D = +263°$. Taking the water of crystallisation in the original salt as being 2·8 per cent., the molecular rotation calculated for the anhydrous salt would be $[M]_D = +270°$, a value which agrees exactly with that of *d*-bromocamphorsulphonic acid.

This result shows that the β-salt is free from the *l*-bromo-acid, and that its low molecular rotation is determined by the presence of hydrindamine; that the base contained in it is externally compensated seems to be a conclusion amply warranted by other facts already recorded.

Isomeric Hydrindamine cis-π-*Camphanates.*

The investigation of these interesting isomerides has been continued and, briefly stated, the results have only served to confirm those previously recorded; samples of the α-isomeride melting at 193° and having a specific rotation $[\alpha]_D = -8°$, when repeatedly crystallised fractionally from alcohol, gradually change in specific rotation and become dextrorotatory, but without any alteration in melting point. The experimental results, however, are very irregular and uncertain, and sometimes two or three recrystallisations fail to bring about any noteworthy change in optical properties.

In the case of these isomerides, more attention has so far been paid to proving that they both contain externally compensated base (Trans., 1900, 77, 909) than to establishing the identity of the acids contained in them, and although the fact that their molecular rotations are practically the same in aqueous solution, indicated the absence

of any isomeric acid, the evidence on this point was not altogether satisfactory. The partial conversion of the β- into the α-salt on evaporating with *dl*-base is a much stronger argument in support of the identity of the acids, but here again the experimental results are very irregular and uncertain; in working with moderate quantities (1·—2 grams) of the β-salt, the solution may be evaporated with base as many as 10 times without any change in melting point of the salt being observed, but on persevering a favourable result is ultimately obtained, and after about 20 operations the melting point of the deposit has usually risen considerably.

The fact that *cis*-π-camphanic acid is formed by the distillation of π-hydroxycamphoric acid at a high temperature (Trans., 1896, **69**, 944) and that consequently the acid used in these experiments might be a mixture of the *d*- and *l*-isomerides owing to partial racemisation having occurred, was a possibility which has not hitherto been discussed, although it has been shown that the acid from the α-salt is identical in melting point and appearance with that of the β-salt; this fact does not exclude the possibility just mentioned because *dl*-*cis*-π-camphanic acid is a mere mixture of the isomerides, and its melting point is practically the same as that of its separate components.

In order to obtain conclusive evidence on this point, samples of the α- and β-salts melting at 193° and 173° respectively were separately decomposed with a solution of hydrogen chloride in aqueous methyl alcohol; the precipitated acids were filtered off, washed well, and dried. Their specific rotations were then determined with the following results:

Acid from α-salt: 0·367 gram was dissolved in water and a few drops of ammonia, the solution diluted to 25 c.c. and examined in a 200 mm. tube: $\alpha_D = -38'$, whence $[\alpha]_D = -21·6°$.

Acid from β-salt: 0·367 gram under exactly the same conditions gave $\alpha_D = -39'$, whence $[\alpha]_D = -22·1°$.

These results show that the salts contain the same acid and thus confirm the conclusion arrived at from the consideration of the data already recorded.

To the Government Grant Committee of the Royal Society the authors desire to express their thanks for a grant which has enabled them to continue this work.

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XLVI.—*Isomeric Hydrindamine Mandelates and Phenylchloracethydrindamides.*

By Frederic Stanley Kipping, Ph.D., D.Sc., F.R.S., and Harold Hall, A.I.C.

Considering the fact that fractional crystallisation of the salts of hydrindamine with so many different optically active acids fails to resolve the base into enantiomorphously related compounds, whilst in some cases the salts are separable into isomeric partially externally compensated substances (Kipping, Trans., 1900, 77, 861, and this vol., p. 430), it seemed interesting to try and obtain some evidence of that asymmetry which the accepted constitution of hydrindamine demands.

For this purpose the hydrindamine salt of racemic mandelic acid was prepared and examined; if the base really is an externally compensated compound it should unite with this acid, forming in solution the four optically different isomerides,

*d*B*d*A; *l*B*l*A; *d*B*l*A; *l*B*d*A,

of which the first and the last pairs might possibly crystallise together, thus forming *two* racemic or externally compensated salts; if separable by fractional crystallisation, the isolation of two such products would serve as confirmatory, if not as conclusive evidence, of the presence of an asymmetric carbon group in hydrindamine.

Experiment showed that the salt actually obtained from hydrindamine and racemic mandelic acid was not separable into isomerides by fractional crystallisation from alcohol or water; consequently, still assuming that the base is externally compensated, it might be concluded either that the salt is actually a crystalline mixture of the *four* optically different isomerides enumerated above, or—which seems more probable—that during its crystallisation the one pair of enantiomorphously related compounds changes into the other, that is to say, *d*B*d*A and *l*B*l*A give *d*B*l*A and *l*B*d*A or *vice versâ*.

The latter view is supported, and the asymmetry of the hydrindamine molecule is established, by the behaviour of the base towards externally compensated phenylchloracetyl chloride, with which it yields two different optically inactive phenylchloracethydrindamides, $C_6H_5\cdot CHCl\cdot CO\cdot NH\cdot C_9H_9$, apparently in equal quantities. These two externally compensated products must of course be represented by *d*Ac*d*B + *l*Ac*l*B and *d*Ac*l*B + *l*Ac*d*B respectively, where Ac represents the radicle $C_6H_5\cdot CHCl\cdot CO$, and B the basic residue, $NH\cdot C_9H_9$.

The apparent difference in the behaviour of the base towards the

externally compensated acid chloride, on the one hand, and the racemic mandelic acid, on the other, is no doubt due to the fact that whereas the four substituted amides cannot undergo any change in solution or during crystallisation, the hydrindamine mandelates are electrolytically and hydrolytically dissociated; in the case of the salts, therefore, the isomeric pairs are mutually convertible

$$d\mathrm{B}d\mathrm{A} + l\mathrm{B}l\mathrm{A} \rightleftarrows d\mathrm{B}l\mathrm{A} + l\mathrm{B}d\mathrm{A},$$

and, on crystallising, only one externally compensated or racemic salt may be obtained.

When pure optically active mandelic acid is neutralised with externally compensated hydrindamine, there is formed a salt which is not separated into isomerides on fractional crystallisation; this salt, therefore, is a partially externally compensated or partially racemic substance and may be represented by $d\mathrm{A}d\mathrm{B} + d\mathrm{A}l\mathrm{B}$.

The great similarity in all except optical properties between this salt and that of the optically inactive acid is very noteworthy; the two compounds are similar in appearance and crystalline character, they have almost the same melting point, and mixtures of the two in different proportions all melt at practically the same temperature as the compounds taken separately.

Now according to the simplest view, the salt of the racemic acid must consist of the two constituents $d\mathrm{A}d\mathrm{B} + l\mathrm{A}l\mathrm{B}$ (or $d\mathrm{A}l\mathrm{B} + l\mathrm{A}d\mathrm{B}$), and the salt of the active acid must contain both $d\mathrm{A}d\mathrm{B}$ and $d\mathrm{A}l\mathrm{B}$, so that in this case a mixture of the three different compounds $l\mathrm{A}l\mathrm{B}$, $d\mathrm{A}d\mathrm{B}$, $d\mathrm{A}l\mathrm{B}$ in different proportions has almost the same melting point as the mixture of equal quantities of any two of its components.

The question whether the melting point affords a criterion for distinguishing between a racemic and an externally compensated compound has recently given rise to much discussion, and the principles underlying the phenomena have been discussed by Bakhuis-Roozeboom (*Zeit. physikal. Chem.*, 1899, **28**, 494). The case above-mentioned, however, appears to be without precedent as regards such optical isomerides, and is therefore of considerable interest.

Even if the completely externally compensated salt $d\mathrm{A}d\mathrm{B}$, $l\mathrm{A}l\mathrm{B}$ of the racemic acid be regarded as a conglomerate or as an isomorphous mixture, it is a curious fact that its melting point should be so close to that of the salt $d\mathrm{A}d\mathrm{B}$, $d\mathrm{A}l\mathrm{B}$ of the active acid, even if the latter is a substance of the same type, because $d\mathrm{A}l\mathrm{B}$ and $l\mathrm{A}l\mathrm{B}$ are different compounds, and the further fact that mixtures of $d\mathrm{A}d\mathrm{B}$, $l\mathrm{A}l\mathrm{B}$, $d\mathrm{A}l\mathrm{B}$ all melt at the same temperature seems to point to the conclusion that these three salts, if separated, would all be found to have almost the same melting point, and to unite in all proportions to form isomorphous mixtures.

The latter conclusion is supported by the behaviour of the salts on crystallisation. When a mixture of the salt of the *dl*- with that of the *d*-acid is submitted to fractional crystallisation, no difference can be detected in the specific rotation of successive deposits; in other words, the three different salts of which such a mixture is composed are deposited together in essentially the same proportion as that in which they exist in solution.

It has recently been shown (this vol., p. 370) that on evaporating a solution of unequal quantities of the hydrindamine salts of *d*- and of *l*-camphor-π-sulphonic acids, the hydrindamine camphorsulphonate is deposited in a larger proportion than that in which it is present in solution; from this fact it was argued that the *dl*-salt is a racemic compound. The analogous mixture of the salts of the *d*- and *l*-mandelic acids does not show this behaviour, and consequently the absence of any racemic or partially racemic compound may be inferred; on the evidence before us, we may therefore conclude that the salts of the active and inactive acids are isomorphous mixtures of two optically different isomerides.

Various interesting questions arise from a consideration of the facts stated above in addition to those concerning the melting point and solubility of mixtures of partially and completely externally compensated salts: whether, for example, it would be possible in any case to isolate *two* externally compensated *salts* by the fractional crystallisation of the product of a racemic acid and a racemic base; employing suitable solvents which would not admit of any dissociation taking place, the reply would probably be in the affirmative, but if not, the further question would then arise as to the possibility of the existence of doubly racemic salts of the type $\left\{\begin{matrix} d\mathrm{A}l\mathrm{B} \\ d\mathrm{A}d\mathrm{B} \end{matrix}\right.$, $\left.\begin{matrix} l\mathrm{A}d\mathrm{B} \\ l\mathrm{A}l\mathrm{B} \end{matrix}\right\}$.

The use of phenylchloracetyl chloride and of other acid chlorides for the detection of asymmetry in amido- and hydroxy-compounds is of course capable of wide application and should prove valuable in many cases which do not yield to other methods; the resolution of such compounds with the aid of optically active acid chlorides should also be possible, and experiments are now being made to test this view.

Externally Compensated Hydrindamine Mandelate.

When racemic mandelic acid is neutralised with an aqueous solution of externally compensated hydrindamine and the solution of the salt concentrated by evaporation, successive crops of crystals of hydrindamine mandelate may be obtained; when these deposits are submitted to further fractional crystallisation, there is no evidence of any separation having occurred, and the properties of the first and last

fractions are in all respects identical; they both melt at 140—141° fairly sharply, sintering slightly at about 138°, and when crystallised from various solvents under the same conditions they give deposits indistinguishable under the microscope. It must be concluded, therefore, that the salt is not separable into isomeric forms by fractional crystallisation.

dl-Hydrindamine *dl*-mandelate is readily soluble in warm water and cold alcohol, moderately so in boiling ethyl acetate, only very sparingly so in boiling chloroform and practically insoluble in cold ether. It seems to be stable at 100°, samples which had been heated on the water-bath for some hours having the melting point 139—140°; in aqueous solution, however, it seems to be very slowly decomposed at 90—100°, the solution becoming turbid, and when the solution is boiled hydrindamine rapidly escapes with the steam. This fact seems to show that the salt is hydrolytically dissociated in aqueous solution to a considerable extent. The salt usually crystallises in flat, transparent, rhomboidal prisms or in concentrically grouped masses of long, prismatic needles; aqueous solutions usually deposit hard, opaque nodules.

Isomeric Externally Compensated Phenylchloracethydrindamides.

Phenylchloracetyl chloride, prepared by treating racemic mandelic acid with phosphorus pentachloride at 160° and distilling under reduced pressure, interacts readily with hydrindamine in ethereal solution, the product separating in colourless crystals mixed with those of hydrindamine hydrochloride; the solution is filtered, the ether evaporated, and the residue mixed with the main bulk of the product, which is then extracted with cold water to separate the hydrochloride.

The crude phenylchloracethydrindamide melts indefinitely at a temperature below 120°, but when repeatedly crystallised from alcohol the melting point of the more sparingly soluble portions gradually rises to 149—150° and there remains constant; this product will be distinguished as the A-isomeride.

The alcoholic mother liquors from the A-isomeride, on spontaneous evaporation, give deposits which are obviously mixtures, but owing to the slight difference in the solubility of the two compounds, the separation of the more readily soluble one is a task of some difficulty. By systematic fractional crystallisation, combined with extraction, and aided by mechanical separation of the two kinds of crystals, it is possible, however, to isolate the readily soluble isomeride, distinguished by B, in moderate quantities. As the separation of the two compounds contained in the intermediate fractions is almost,

if not quite, impossible, it cannot be stated with certainty that the two isomerides are formed in equal quantities; but this appears to be the case, and no doubt is so.

On analysing the two substituted amides by Carius' method, the following results were obtained:

A-Isomeride: 0·1546 gave 0·0795 AgCl. Cl = 12·7.
B-Isomeride: 0·1805 „ 0·0932 AgCl. Cl = 12·7.
$C_6H_5 \cdot CHCl \cdot CO \cdot NH \cdot C_9H_9$ requires Cl = 12·4 per cent.

A-*Isomeride.*—This compound crystallises from alcohol or acetic acid in large, flat, transparent and well-defined oblong plates, which are exceedingly brittle; it is practically insoluble even in boiling water, and only sparingly soluble in ether, but it dissolves fairly readily in boiling alcohol, and freely in cold chloroform or acetic acid. It is very stable, and is not decomposed to an appreciable extent by boiling water or moderately concentrated hydrochloric acid, but is slowly hydrolysed by boiling diluted sulphuric acid, at the same time suffering secondary decomposition and giving rise to tarry products.

B-*Isomeride.*—When this compound is crystallised from alcohol, it is deposited in long, transparent prisms, aggregated in rosette-like masses, which are easily distinguished from the plates of the A-isomeride; in behaviour towards solvents it resembles the latter very closely, but is generally more readily soluble. It melts at 123—124°.

Both isomerides, of course, are optically inactive.

Partially Externally Compensated Hydrindamine Mandelate.

The examination of the salt formed from hydrindamine and active mandelic acid was undertaken principally with the object of ascertaining whether this compound would be separable into isomeric partially racemic salts analogous to the hydrindamine bromocamphorsulphonates; experiment showed that this was not so, nor is the salt resolvable into isomerides representing compounds of the enantiomorphously related bases; it must therefore be regarded as a partially externally compensated or racemic substance.

The *d*-mandelic acid which was employed was prepared from the racemic acid by fractional crystallisation of its salt with cinchonine according to the directions of Rimbach (*Ber.*, 1899, **32**, 2385), and a determination of its specific rotation gave the following result:

0·5 gram dissolved in water and the solution diluted to 25 c.c., gave, in a 200 mm. tube: $\alpha_D = 6°1'$, whence $[\alpha]_D = +150·5°$.

The hydrindamine salt, obtained by neutralising an alcoholic solution of this acid with the base, was first separated into a number of fractions by gradually concentrating the solution, and these deposits were

then further crystallised systematically from ethyl alcohol; during this process, there were no signs of any separation having occurred, and on comparing the properties of the first and last fractions no difference of any kind could be observed.

The specific rotations of the two fractions were also identical within the limits of experimental error, as shown by the following determinations:

First fraction: 0·5 gram dissolved in 99·8 per cent. ethyl alcohol, the solution diluted to 25 c.c. and examined in a 200 mm. tube, gave $\alpha_D = +2°6'$, whence $[\alpha]_D = +52·5°$.

Last fraction: 0·5 gram; same conditions; $\alpha_D = +2°4'$; $[\alpha]_D = +51·7°$.

Experiments, with water as solvent, other conditions remaining the same, gave the following results:

First fraction: $\alpha_D = +2°34'$; $[\alpha]_D = +64·1°$; $[M]_D = +183°$.
Last fraction: $\alpha_D = +2°29'$; $[\alpha]_D = +62·5°$; $[M]_D = +178°$.

The molecular rotation of mandelic acid, calculated from the specific rotation of the acid, is $[M]_D = +228°$ and the difference between this value and that obtained in the case of the hydrindamine salt may be attributed to incomplete dissociation; the practical identity of the specific rotations of the two fractions of the salt shows that no resolution of the base has occurred, and this is confirmed by the fact that the base liberated from the salt after fractional crystallisation has been carried out is optically inactive; this salt, therefore, is partially externally compensated.

Melting Points of the Partially and Completely Externally Compensated Hydrindamine Mandelates.

When the salt prepared from racemic mandelic acid is compared with that obtained from the *d*-acid by crystallising the two preparations separately from a given solvent and then examining the crystals under a microscope, there is no constant difference in behaviour except perhaps that the salt of the racemic acid forms rather more well-defined crystals than those of the isomeride; the solubilities of the two salts in various solvents also appear to be very much the same. On heating, the two compounds melt almost simultaneously at 138—140·5°, both sintering very faintly at about 137°, and a finely divided mixture of the two shows the same behaviour; various mixtures containing different proportions of the two salts were examined, but they all behaved in the same way.

As the melting points of the two salts are not very sharp, it is difficult to decide whether they are quite the same or not; from the

results of many observations, we are inclined to conclude that the melting point of the inactive acid (140—141·5°) is about 1·5° higher and rather more definite than that of the active acid.*

On mixing samples of the partially and completely externally compensated salts and then fractionally crystallising from alcohol, the several fractions all melt at the same temperature, namely, at 138—140·5°.

Crystallisation of a Mixture of Partially and Completely Externally Compensated Hydrindamine Mandelates.—The fact that the melting point of mixtures of these two salts in different proportions is so close to that of both the components makes it impossible to tell, without optical examination, whether any separation occurs when such mixtures are fractionally crystallised; considering the somewhat close relationship between the two compounds, it seemed interesting to ascertain whether such a separation could be accomplished.

For this purpose, a mixture of 48·6 per cent. of the salt of the *dl*-acid and 51·4 per cent. of that of the *d*-acid was prepared; the specific rotation of this mixture in a 2 per cent. solution in ethyl alcohol was found to be $[\alpha]_D = +28·2°$, whereas the value calculated from the observed specific rotation of the salt of the pure *d*-acid is $[\alpha]_D = +26·8°$ under the same conditions. The mixture was then dissolved in alcohol and by cooling the solution a considerable deposit was obtained; this was separated, recrystallised from a mixture of ethyl alcohol and ethyl acetate, and then examined. 0·5 gram dissolved in ethyl alcohol and the solution diluted to 25 c.c. gave, in a 200 mm. tube, $\alpha_D = +1°6'$; $[\alpha]_D = +27·5°$.

This result indicated that no separation had occurred; the deposit was therefore crystallised again twice from ethyl alcohol, until it had been reduced to about 25 per cent. of the weight of the original mixture; its specific rotation was then determined under the same conditions as before, the result being $\alpha_D = +1°5\frac{1}{2}'$, whence $[\alpha]_D = +27·3°$.

The mother liquors from the first deposit were also evaporated and successive crops of crystals separated until only about 8 per cent. of the original mixture remained in the solution, which was finally evaporated almost to dryness. The specific rotation of the fraction finally obtained was found to be $[\alpha]_D = +30·2°$, but as the sample was slightly brown the experimental error might easily account for the observed difference between this and the pure specimen of the first deposit with which the more trustworthy result was obtained. It may be concluded,

* When rapidly precipitated from methyl alcoholic solution by the addition of ether and then placed on porous earthenware, the salt of the active acid melts to a great extent at about 130—132°; the salt of the inactive acid, prepared in a similar manner, also shows distinct signs of melting at a lower temperature than usual. This behaviour does not seem to be due to the presence of solvent, as the salt of the inactive acid keeps its low melting point even after 12 hours exposure to the air.

therefore, that no appreciable separation occurs when a mixture of the salts is submitted to fractional crystallisation.

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XLVII.—*Organic Derivatives of Silicon. Triphenylsilicol and Alkyloxysilicon Chlorides.*

By F. Stanley Kipping, Ph.D., D.Sc., F.R.S., and Lorenzo L. Lloyd.

Although this research was commenced nearly three years ago (compare Proc., 1899, **15**, 174), its principal object, namely, the preparation of an optically active silicon compound, has not been attained; under these circumstances, it might perhaps have been better to postpone publication until more progress had been made, but as one of us has been obliged to abandon the investigation, we wish to place on record a brief account of the results obtained up to the present.

Our first attempts were directed towards the preparation of derivatives of silicon tetraphenyl, a compound which is obtained with comparative ease by the method described by Polis (*Ber.*, 1885, **18**, 1542). This substance, however, proved to be unsuitable for our purpose; although it can be nitrated without much difficulty (Polis, *loc. cit.*), the product did not crystallise, and appeared to be a mixture which was not easily resolvable into its components. Treatment of the silicon tetraphenyl with halogens under various conditions also failed to yield satisfactory results, and numerous attempts to prepare sulphonic derivatives were equally unsuccessful, the principal products of the action of ordinary sulphonating agents being silica and benzenesulphonic acid or diphenylsulphone; phosphorus pentachloride, hydrogen chloride, and other reagents were tried, but we found it impossible to isolate any suitable product even when reaction occurred. Attention was next directed to the bye-products which are formed in the preparation of silicon tetraphenyl, and from these we were able to isolate small quantities of triphenylsilicol, $(C_6H_5)_3Si{\cdot}OH$, a compound which is formed from the triphenylsilicium chloride contained in the mother liquors from the silicon tetraphenyl. Triphenylsilicol was first obtained by Polis (*loc. cit.*) by strongly heating silicon tetraphenyl with phosphorus pentachloride and treating the

product with dilute ammonia; as it crystallises well and already contains two different groups and is more readily soluble than the tetraphenyl derivative, we tried to obtain it in larger quantities by altering the proportions of silicon tetrachloride, chlorobenzene, and sodium used in the preparation of silicon tetraphenyl; the results, however, were not very satisfactory, and as we found that the silicol was of little use for our main object, we did not persevere with these experiments.

In attempting to nitrate triphenylsilicol we found that this alcohol is converted into an ether with extraordinary readiness; this change takes place when the alcohol is heated with a 10 per cent. solution of hydrogen chloride in acetic acid. The product, di-triphenylsilicyl ether, $[(C_6H_5)_3Si]_2O$, is a very stable compound although it is slowly hydrolysed by boiling alcoholic potash.

Various substances other than triphenylsilicol were isolated from the bye-products obtained in the preparation of silicon tetraphenyl, but they were of little interest, except perhaps one compound which seems to be diphenylsilicium ketone, $(C_6H_5)_2SiO$; this substance bears little, if any, resemblance to benzophenone, and is possibly a polymeride of high molecular weight.

Fatty alkyl derivatives of silicon have hitherto been obtained only by heating silicon tetrachloride with the zinc alkyl compounds, a method which is inconvenient and troublesome. We therefore studied the application of Fittig's reaction to the preparation of such compounds, and found that silicon tetraethyl could be prepared by this method with comparative facility, as a very fair yield is obtained when a mixture of silicon tetrachloride and ethyl bromide or iodide is digested with sodium in ethereal solution in presence of traces of ethyl acetate.

Little has been done with this alkyl compound up to the present, as other experiments which offered a possibility of more immediate success have been in progress.

Starting from silicon tetrachloride, we tried to prepare asymmetric derivatives directly by the successive displacement of the chlorine atoms by three different groups; these attempts were successful, and products, such as phenoxymethoxyethoxysilicon chloride, were obtained by the following series of interactions:

$$\begin{aligned} SiCl_4 + PhOH &= SiCl_3{\cdot}OPh + HCl \\ SiCl_3(OPh) + MeOH &= SiCl_2(OMe){\cdot}OPh + HCl \\ SiCl_2(OPh)(OMe) + EtOH &= SiCl(OPh)(OMe){\cdot}OEt \end{aligned}$$

Although the final product of these reactions contains the desired asymmetric silicon atom, we were unable to resolve it into enantiomorphously related components, owing to its sensitiveness towards moisture; when treated with the dry silver salt of an optically active

acid in dry ethereal solution, interaction took place, apparently in the normal manner, but the product decomposed even when kept over sulphuric acid. Other experiments in which aniline and toluidine were employed in the place of phenol or the alcohols in the above reaction gave products which were equally unstable. We next tried treating the phenoxymethoxyethoxysilicon chloride with menthol, in the hope that by displacement of the chlorine by the menthyl radicle we might obtain a crystalline product which would be directly resolvable into the menthyl derivatives of two enantiomorphously related silicon compounds by fractional crystallisation; unfortunately, this product did not solidify even when cooled to $-40°$, and it was also readily decomposed by water.

For the estimation of the silicon in some of the compounds which were examined, we employed a new and very simple method, namely, treatment with concentrated sulphuric acid followed by ignition; this method gives very satisfactory results except in the case of volatile, stable compounds such as silicon tetraethyl.

Experimental.

Preparation of Silicon Tetraphenyl.—The preparation of silicon tetrachloride by Gattermann's method, and the conversion of this substance into silicon tetraphenyl under the conditions laid down by Polis (*loc. cit.*), need not be described. We may state, however, that when ether is used as solvent in the latter preparation the reaction takes place spontaneously, and usually so vigorously that the contents of the flask require cooling in ice water, so that the addition of ethyl acetate is unnecessary; the interaction proceeds gently during about 8 hours and is completed by heating on the water-bath for about 1 hour. The product is then separated by filtration, washed with alcohol and water consecutively, and dried. The yield is almost theoretical.

The nitration of silicon tetraphenyl has been carried out by Polis (*loc. cit.*), and he describes the product as being amorphous; following his directions, we also obtained a substance from which nothing crystalline, except traces of unchanged silicon tetraphenyl, could be isolated. On fractional precipitation from acetic acid by addition of water, we obtained it in colourless, flocculent, apparently amorphous particles, but successive fractions had not the same melting point, and on analysis gave nitrogen varying from about 12 to 15 per cent. Silicon tetranitrotetraphenyl requires 10·9 per cent. The crude preparation did not seem to afford a base when treated with any of the ordinary agents which reduce nitro-compounds, and when boiled with

caustic alkalis it seemed to be completely decomposed into silica and nitrobenzene.

Nitric acid alone seems to have no action on silicon tetraphenyl at the ordinary temperature, and in presence of varying quantities of sulphuric acid either nitration is very incomplete or a product similar to that just described is obtained.

A solution of hydrogen chloride in acetic acid slowly decomposes silicon tetraphenyl at 130—140°, giving benzene and traces of triphenylsilicol; at higher temperatures, silica and benzene seem to be the only products.

When silicon tetraphenyl is cautiously added to 30 per cent. anhydrosulphuric acid, it slowly dissolves, giving a brownish, very viscous solution, which, when poured on to powdered ice, does not deposit silica; after neutralising with barium carbonate, a solution is obtained which on evaporation deposits barium benzenesulphonate.

Silicon tetraphenyl dissolves readily in well-cooled chlorosulphonic acid with evolution of hydrogen chloride; the product consists principally of a mixture of benzenesulphonic chloride and diphenylsulphone.

When silicon tetraphenyl is dissolved in acetic anhydride and treated with anhydrosulphuric acid, it gives benzenesulphonic acid and soluble silicic acid; in order to prevent such a decomposition, we tried to sulphonate with sulphur trioxide, the silicon tetraphenyl being mixed with dry sand in order to moderate the action. Under these conditions, we recovered a considerable quantity of silicon tetraphenyl, but the portion soluble in water again gave an acid which appeared to consist entirely of benzenesulphonic acid.

Phosphorus pentachloride has no action on melted silicon tetraphenyl at 250°, and very little action when the two substances are heated together in a sealed tube at 250—260° for 12 hours, only small quantities of triphenylsilicyl chloride being formed; as most of the tubes burst at this temperature, the experiments were discontinued.

Triphenylsilicol and its Derivatives.

The ethereal filtrate from the mixture of silicon tetraphenyl, sodium chloride, and unchanged sodium, obtained in the preparation of the first-named compound, usually contains small quantities of chlorobenzene, diphenyl, and various other substances which are formed as bye-products; on evaporating the ether, there remains an oily liquid from which the chlorobenzene can be separated by distillation under atmospheric pressure. The thick, oily residue, when distilled under 10 mm. pressure, gives first a fraction passing over

between 120° and 160° which consists largely of diphenyl, and then very little distils until the temperature rises to about 210°; between this temperature and about 260°, a thick, almost colourless liquid passes over, and a non-volatile, pasty mass containing a large quantity of combined silicon remains in the distilling flask.

The fraction collected between 210° and 260° seems to consist of a mixture of triphenylsilicyl chloride, triphenylsilicol, and silicon tetraphenyl, and when, owing to absorption of moisture during manipulation of the bye-products, most of the first-named compound has been converted into the second, the latter separates in crystals often in such quantities that the distillate becomes nearly solid. This crystalline product may be separated by filtration, washed with a mixture of light petroleum and ether, and then repeatedly crystallised, to free it from silicon tetraphenyl. As an alternative method, the whole of the fraction collected between 210° and 260° may be boiled for a short time with a little alcoholic soda to decompose the chloride, in which case the silicon tetraphenyl is separated by careful precipitation with water, and the crude triphenylsilicol, deposited slowly from the alcoholic filtrate, is purified by crystallisation from a mixture of ether and light petroleum. The compound obtained in this way melts at 148° and has been briefly described by Polis (*loc. cit.*), who prepared it by heating silicon tetraphenyl with phosphorus pentachloride and treating the resulting chloride with dilute ammonia; as the melting point of triphenylsilicol according to him is 139—141°, the nature of our preparation seemed doubtful until established by the following analyses:

0·1618 gave 0·4665 CO_2 and 0·0859 H_2O. C = 78·6; H = 5·9.
0·21 „ 0·0451 SiO_2. Si = 10·02.
$C_{18}H_{16}OSi$ requires C = 78·2; H = 5·9; Si = 10·14 per cent.

Triphenylsilicol crystallises from a mixture of ether and light petroleum in well-defined, massive, transparent prisms and is readily soluble in acetic acid, benzene, chloroform, carbon disulphide, ether, or alcohol.

As only very small quantities of triphenylsilicol were obtained from the bye-products resulting from the preparation of silicon tetraphenyl in the manner described by Polis, many experiments were made in order to ascertain whether the yield of this alcohol could be increased by altering the proportions of silicon tetrachloride, chlorobenzene, and sodium; it was found, however, that the reaction expressed by the equation,

$$SiCl_4 + 3C_6H_5Cl + 6Na = Si(C_6H_5)_3Cl + 6NaCl,$$

cannot be brought about except to a very limited extent; working with these relative quantities, 15 grams of silicon tetrachloride give

only about 2 grams of the crude product boiling at 210—260° under 10 mm. pressure, and even when smaller proportions of chlorobenzene and sodium are used, silicon tetraphenyl is always the principal product, a correspondingly larger amount of silicon tetrachloride remaining unchanged.

Triphenylsilicol is insoluble in 30 per cent. anhydrosulphuric acid, but dissolves in ice-cold chlorosulphonic acid with evolution of hydrogen chloride. The only products which were isolated from this solution were diphenylsulphone and benzenesulphonic acid, the latter in the form of its sodium salt. When triphenylsilicol is dissolved in chloroform and then treated with chlorosulphonic acid, the results are similar, diphenylsulphone and benzenesulphonic chloride being obtained together with some unaltered triphenylsilicol.

Triphenylsilicyl acetate, $(C_6H_5)_3SiO{\cdot}CO{\cdot}CH_3$.—Acetic anhydride, even in the presence of zinc chloride, has no action on triphenylsilicol, but the acetyl derivative can be obtained by boiling the alcohol with acetyl chloride until it has passed into solution. One gram of silicol requires boiling about 2 hours with 10 c.c. of acetyl chloride before the change is complete. The liquid is then evaporated, and the residue crystallised from light petroleum (b. p. 60—80°), in which it is readily soluble on boiling, and from which it is deposited in long, thick prisms melting at 91·5°.

0·1623 gave 0·450 CO_2 and 0·0832 H_2O. C = 75·62 ; H = 5·75.
0·3210 „ 0·0607 SiO_2. Si = 8·82.
$C_{20}H_{18}O_2Si$ requires C = 75·78 ; H = 5·66 ; Si = 8·8 per cent.

Triphenylsilicyl acetate is readily soluble in benzene, chloroform, carbon disulphide, alcohol, or acetic acid, but only sparingly so in cold light petroleum ; it decomposes slowly on exposure to air and is rapidly hydrolysed by boiling dilute alcohol.

Triphenylsilicyl chloride, $Si(C_6H_5)_3Cl$.—This compound is sometimes obtained directly from the mixture of bye-products already referred to (p. 452) after distilling off the chlorobenzene under atmospheric and then fractionating the residue under 10 mm. pressure ; the fraction collected between 220° and 240° sometimes solidified to a mass of colourless crystals, which were readily soluble in light petroleum, and on evaporating this solution, triphenylsilicyl chloride was deposited in an almost pure condition. It may also be obtained, but with great difficulty, by heating silicon tetraphenyl with phosphorus pentachloride as described by Polis.

0·3006 gave 0·1447 AgCl. Cl = 11·93.
$C_{18}H_{15}ClSi$ requires Cl = 12·06 per cent.

Triphenylsilicyl chloride crystallises from light petroleum in trans-

parent prisms, melts at 88—89°, and dissolves freely in most ordinary solvents; it does not fume in the air, but is readily hydrolysed by dilute alcoholic potash.

Di-triphenylsilicyl Ether, $[Si(C_6H_5)_3]_2O$.

Triphenylsilicol dissolves in concentrated nitric acid, but only very slowly, giving a solution from which a nitro-compound is not precipitated on the addition of water. It dissolves more readily in a mixture of nitric acid (1 part) and sulphuric acid (3 parts), and on pouring the solution into water an oil which contains nitrogen and is soluble in potash is precipitated; when, however, it is heated with nitric acid in acetic acid solution, it is converted into triphenylsilicyl ether. This compound is easily prepared by dissolving triphenylsilicol in acetic acid, heating to boiling, and then adding concentrated nitric acid drop by drop until the mixture becomes turbid; the solution, which gradually acquires a deep red colour, soon deposits crystals which are filtered off and recrystallised from acetic acid.

0·2 gave 0·5947 CO_2 and 0·1002 H_2O. C = 81·1; H = 5·56.
0·2 „ 0·5920 CO_2 „ 0·0978 H_2O. C = 80·78; H = 5·43.
0·2 „ 0·450 SiO_2. Si = 10·5.
$C_{36}H_{30}OSi_2$ requires C = 80·9; H = 5·6; Si = 10·48 per cent.

Di-triphenylsilicyl ether crystallises in small, shining plates melting at 222°. It is practically insoluble in methyl alcohol and cold acetic acid, and only very sparingly soluble in ethyl alcohol, but it dissolves more readily in acetic anhydride and is very soluble in ether or benzene. It gradually goes into solution in boiling alcoholic potash, passing into triphenylsilicol.

Triphenylsilicyl ether can also be obtained by boiling a solution of triphenylsilicol in a mixture of acetic acid and 10 per cent. hydrochloric acid for about 8 hours, and then crystallising the deposit from acetic acid; also by boiling for a considerable time a solution of triphenylsilicol in methyl alcohol and concentrated hydrochloric acid.

Diphenyl Silicone, $SiPh_2O$.

The residue left after distilling off the triphenylsilicol (p. 453) from the crude bye-product, does not volatilise at 280° under 10 mm. pressure, and solidifies on cooling to a pale yellow, vitreous mass; when boiled with alcoholic potash, traces of triphenylsilicol and some silicon compound which is precipitated again on the addition of hydrochloric acid are dissolved, and there remains a considerable quantity of a neutral substance. The latter, after having been dried, is extracted with carbon disulphide, and light petroleum (b. p. 40—60°)

added to the extract; this precipitates a sticky mass, which is purified by dissolving it in ether and precipitating with alcohol.

The substance thus obtained melts, not sharply, at about 109° and from the following analysis it would seem to be diphenyl silicone, but we were unable to obtain it in a crystalline condition, so that its nature is not definitely established.

0·2082 gave 0·5526 CO_2 and 0·0982 H_2O. C = 72·38; H = 5·24.
0·2 ,, 0·0616 SiO_2. Si = 14·38 per cent.
$C_{12}H_{10}OSi$ requires Si = 14·64; C = 72·72; H = 5·05 per cent.

This compound is practically insoluble in acetic acid, alcohol, or light petroleum, but readily soluble in ether, chloroform, benzene, or carbon disulphide.

Preparation of Silicon Tetraethyl, $Si(C_2H_5)_4$.

The preparation of silicon tetraethyl by the interaction of zinc ethyl and silicon tetrachloride being a very troublesome and expensive process, we made experiments to find out whether this compound could be obtained by the application of Fittig's reaction. For this purpose, silicon tetrachloride (10 grams) and ethyl bromide (26 grams) were dissolved together and added to sodium wire (12 grams) in dry ether; as no reaction occurred after heating on the water-bath for some time, a little ethyl acetate was added, whereupon change set in and proceeded very gently, sodium bromide separating; after digesting for two days, the solution was filtered, the ethereal filtrate and washings evaporated, and the residual liquid fractionated. It began to boil at about 100°, and the thermometer rose fairly quickly to 140°, but between 140° and 160° a considerable quantity passed over; only a small portion distilled between 160° and 170°. The fraction collected between 140° and 160° (about 5 grams) was dissolved in a little ether, washed with dilute sodium carbonate to remove acid, dried, and redistilled, the portion boiling at 154—155° being collected separately. This fraction (about 3 grams) consisted of silicon tetraethyl practically free from impurity, as shown by the following analysis:

0·2005 gave 0·4878 CO_2 and 0·2527 H_2O. C = 66·31; H = 14·00.
$C_8H_{20}Si$ requires C = 66·66; H = 13·88 per cent.

The silicon could not be easily estimated by heating with sulphuric acid, as in the case of the other silicon compounds, which were analysed in this way; different determinations were made, but the results were not concordant, being 18·01 and 17·45 per cent. of silicon respectively, the calculated amount being 19·44 per cent.

The lack of agreement between these two results, and the low per-

centage of silicon actually found, may be ascribed to volatilisation of the silicon tetraethyl.

The effect of substituting ethyl iodide for bromide in the method of preparation just described is not advantageous; quantities corresponding with the above were mixed with dry ether and then heated on the water-bath, but action took place very slowly, and the solution turned dark brown; after heating for 3 days, the product was isolated as before, but from 20 grams of silicon tetrachloride we only obtained about 5 grams of silicon tetraethyl boiling at 154—155°; the purity of this preparation is shown by the following analysis:

0·2136 gave 0·5208 CO_2 and 0·2684 H_2O. C = 66·48; H = 13·98.
$C_8H_{20}Si$ requires C = 66·66; H = 13·88 per cent.

Phenoxymethoxysilicon Dichloride, $SiCl_2(OMe)\cdot OPh$.—This compound was obtained by adding a solution of phenol (1 mol.) in ether drop by drop to an ethereal solution of silicon tetrachloride (1 mol.), and then slowly running in an ethereal solution of methyl alcohol (1 mol.); after evaporating the ether, the product was fractionated under atmospheric pressure, and the portion passing over between 210° and 220° collected separately; this formed the principal portion of the crude product, and after further fractionation it gave a colourless, mobile liquid boiling at 216° under 752 mm. pressure. On analysis, the following result was obtained:

0·2201 gave 0·2864 AgCl. Cl = 32·18.
$C_7H_8O_2Cl_2Si$ requires Cl = 31·8 per cent.

Phenoxymethoxysilicon dichloride boils under the ordinary pressure without appreciable decomposition; it is very readily decomposed by water, giving silica, hydrochloric acid, phenol, and methyl alcohol.

Phenoxymethoxyethoxysilicon chloride, $SiCl(OMe)(OEt)\cdot OPh$.—This compound is easily prepared by slowly adding an ethereal solution of ethyl alcohol to an ethereal solution of the preceding compound; after evaporating the ether and repeatedly fractionating the product under atmospheric pressure, it is obtained as a colourless, oily liquid boiling at 241°.

0·3201 gave 0·1896 AgCl. Cl = 15·34.
$C_9H_{13}O_3ClSi$ requires Cl = 15·29 per cent.

This substance is decomposed by water with separation of silica, but not with very great rapidity; although it seemed relatively stable in presence of moisture, attempts to displace the chlorine atom by an acid radicle were unsuccessful. When digested with dry silver bromocamphorsulphonate in ethereal solution, silver chloride separated, and the

ethereal solution, on evaporation in a desiccator, gave an oil which, however, seemed to be almost immediately resolved into bromocamphorsulphonic acid, phenol, and other products.

Methoxyethoxysilicon Dichloride, $SiCl_2(OMe)\cdot OEt$.—As it seemed possible that a more stable substance could be obtained by substituting a fatty alkyl group for phenol in the preceding substance, we treated silicon tetrachloride first with methyl alcohol (1 mol.), and then with ethyl alcohol (1 mol.), in ethereal solution; the product, after repeated fractional distillation, afforded a colourless liquid boiling at 128° under the ordinary pressure. On analysis, the following result was obtained:

0·1625 gave 0·2679 AgCl. Cl = 40·78.

$C_3H_8O_2Cl_2Si$ requires Cl = 40·57 per cent.

Methoxyethoxyisobutyloxysilicon chloride, $SiCl(OMe)(OEt)\cdot OBu^{\beta}$.—On treating the preceding compound with *iso*butyl alcohol under the conditions previously described, interaction took place readily, and the principal product, isolated by fractional distillation, boiled at 159—160° under atmospheric pressure.

0·3724 gave 0·2475 AgCl. Cl = 16·42.

$C_7H_{17}O_3ClSi$ requires Cl = 16·7 per cent.

Methoxyethoxy*iso*butyloxysilicon chloride is a colourless, fairly mobile oil, but it seems to be just as readily decomposed by water as the phenoxy-derivative; it interacts with amino-compounds in ethereal solution, but the products are also unstable towards water.

Phenoxyethoxymethoxyanilinosilicon, $Si(OMe)(OEt)(OPh)\cdot NHPh$.—In order to ascertain whether a stable anilino-derivative could be obtained from the phenoxyethoxymethoxysilicon chloride, a considerable quantity of the latter was gradually treated with aniline (2 mols.) in ethereal solution; the aniline hydrochloride which was free from silica was then separated by filtration, and the ethereal solution evaporated. The residue, a thick oil, crystallised in colourless needles when cooled with a mixture of carbon dioxide and ether, but as it melted again at a very low temperature, and was readily decomposed by water with separation of silica, it was not examined further.

Phenoxyethoxymethoxymenthoxysilicon, $Si(OMe)(OEt)(OPh)\cdot OC_{10}H_{19}$, was prepared by treating the phenoxymethoxyethoxysilicon chloride described above with menthol (1 mol.) in ethereal solution, and was obtained as a thick, colourless oil which did not solidify when cooled with ether and carbon dioxide; it was readily decomposed by water, giving silica, menthol, phenol, and the alcohols.

We beg to express our thanks to the Government Grant Committee of the Royal Society for a grant by which part of the cost of this work has been met.

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Nottingham.

XLVIII.—*The Bacterial Oxidation of Formates by Nitrates.*

By Walter Charles Cross Pakes and Walter Henry Jollyman.

In previous papers (this vol., pp. 322, 386), we have described the action of certain bacteria on sodium formate, and shown that the formic acid is decomposed into equal volumes of carbon dioxide and hydrogen; we have also shown that at least one bacterium has the power of liberating free oxygen from nitrates.

It was suggested to us by Mr. Pope that if our facts were correct a bacterium which attacked both formate and nitrate would probably produce no hydrogen from the formate, as this substance would be oxidised by the oxygen from the nitrate, when the organism was grown in presence of both salts. This has proved to be the case.

In order to test this theory, our first experiment was made with the *Bacillus coli communis* because this organism decomposes formate and powerfully reduces nitrate. Some meat extract to which was added 1 per cent. of peptone and 0·5 per cent. of common salt was carefully neutralised and to it was added exactly 1 per cent. of sodium formate. The medium was then divided into two portions and to one of these exactly 1 per cent. of potassium nitrate was added. After filtration, these portions were filled into flasks, sterilised, inoculated with the *B. coli communis*, and connected under anaerobic conditions to the gas receiver already described (this vol., p. 323). The results were as follows:

The flask containing only the formate yielded in five days 354·4 c.c. of gas (72·3 c.c. per 100 c.c. of medium) consisting of 12·5 per cent. of carbon dioxide and 87·5 per cent. of hydrogen.

The flask containing both formate and nitrate yielded no gas at all at the end of seven days. The medium was strongly alkaline, 100 c.c. requiring 105 c.c. of *N*/10 sulphuric acid to bring the reaction back to that of the medium before the growth had taken place.

In these experiments, the gas was withdrawn from the receiver at the end of the first, fourth, and fifth days; further experiments

differing from them only in the fact that no analysis was made of the gas until after the lapse of seven days, gave similar results.

The flask containing only formate yielded 49·2 c.c. of gas per 100 c.c. of medium consisting of 11·2 per cent. of carbon dioxide and 88·8 per cent. of hydrogen.

The flask containing both formate and nitrate yielded no gas.

Experiments upon similar lines were then conducted with the *B. enteritidis* of Gärtner instead of with the *B. coli communis*. Three flasks were taken, one containing only formate and two containing both formate and nitrate. The results were as follows :

The flask containing only formate yielded in six days 114·8 c.c. of gas per 100 c.c. of medium, consisting of 19·7 per cent. of carbon dioxide and 80·3 per cent. of hydrogen.

From neither of the flasks containing both formate and nitrate was there any trace of gas produced in six days.

The oxidation effected may be expressed by the equation :

$$H{\cdot}CO_2Na + NaNO_3 = NaHCO_3 + NaNO_2.$$

The presence of sodium hydrogen carbonate in all the media was proved by the fact that carbon dioxide was liberated on adding sulphuric acid ; the absence of normal carbonate was shown by the acidity of the medium to phenolphthalein ; abundant evidence of nitrite was also obtained.

In the above experiments, the nitrate is in excess as regards the formate, so that sufficient oxygen is liberated from the nitrate by its conversion into nitrite to convert the sodium formate into sodium hydrogen carbonate. When, however, the formate is in considerable excess as compared with the nitrate, gas is produced which on analysis is found to contain carbon dioxide and nitrogen. We have not yet performed a sufficient number of experiments to enable us to arrive at a conclusion as to the manner in which the decomposition is effected, but we hope to show this in a later paper.

If instead of formate we use *d*-glucose, the hydrogen evolved from the *d*-glucose is oxidised by the nitrate, and, as with formate, the gas evolved is found to consist of carbon dioxide and nitrogen (if the nitrate is in excess) and of carbon dioxide, nitrogen, and hydrogen if the *d*-glucose is in excess.

The following experiments illustrate this fact :

Meat extract to which 2 per cent. of *d*-glucose, 0·5 per cent. of sodium formate, 0·5 per cent. of common salt, and 1 per cent. of peptone were added, was neutralised with *N*-sodium hydroxide, filtered, and divided into two portions. The first portion was placed in a flask, sterilised, inoculated with the *B. coli communis*, and connected to the gas receiver. To the second portion 1 per cent. of potassium nitrate

was added, after which it was treated in exactly the same manner as the first portion.

The *d*-glucose-formate medium in six days yielded, per 100 c.c. of medium, 286·5 c.c. of gas, which contained 44·6 per cent. of carbon dioxide and 56·4 per cent. of hydrogen.

The *d*-glucose-formate-nitrate medium yielded 76·6 c.c. of gas per 100 c.c. of medium, and this was found to contain 67·2 per cent. of carbon dioxide, traces of hydrogen, and (by difference) 32·8 per cent. of nitrogen.

When either the *B. enteritidis* of Gärtner or the *Pneumobacillus* of Friedländer was substituted for the *B. coli communis*, the result was the same, carbon dioxide and hydrogen were evolved from *d*-glucose-formate medium, and carbon dioxide and nitrogen from *d*-glucose-formate-nitrate medium.

These three bacteria, as has been stated, decompose both formate and nitrate; we decided therefore to ascertain, if possible, the result of growing a bacterium which only attacks one of these in a medium containing both. One bacterium, the *B. pyocyaneus*, decomposes nitrate but not formate, and when this organism is grown upon formate-nitrate medium the gas evolved consists of carbon dioxide and nitrogen, the only difference found between the action on this medium and on the nitrate medium being that in this case less carbon dioxide is evolved than from nitrate alone.

We have as yet been unable to find a bacterium which decomposes formate without reducing nitrate, and further experiments are being made with this object.

XLIX.—*The Action of Acetylchloro- and Acetylbromo-aminobenzenes on Amines and Phenylhydrazine.*

By F. D. Chattaway and K. J. P. Orton.

The action of chloro- and bromo-amino-derivatives on other compounds has been but little investigated, chiefly owing to the fact that these substances either have been prepared with difficulty, or do not easily lend themselves to manipulation. Some of the acetylchloro- and acetylbromo-aminobenzenes recently described by us are, however, extremely easily obtained in a pure and dry state, and can be used for studying the reactions of this group with other classes of compounds.

In this paper we propose to consider the action of these substituted aminobenzenes on amines and phenylhydrazine.

The earliest experiments of this nature were those of Hofmann (*Ber.*, 1882, **15**, 407), who found that *s*-tribromoaniline was formed in the action of acetbromoamide on aniline.

Bender later (*Ber.*, 1886, **19**, 2272) obtained 2 chloro-*p*-nitroaniline by the action of acetylchloroaminobenzene on *p*-nitroaniline, whilst Hentschell (*Ber.*, 1897, **30**, 2643) recently tried the action of nitrogen chloride (NCl_3) dissolved in benzene on aniline and on monomethylaniline, from both of which *s*-trichloro-derivatives were obtained. A small quantity of the aniline was converted into azobenzene.

All amines react readily with the acetylchloro- and acetylbromoaminobenzenes. The course of the reaction can generally be followed best by using solutions of the dry reagents in anhydrous solvents such as chloroform or benzene. Other solvents, such, for example, as alcohol, acetic acid, or ether, may be used and do not affect the general course of the reaction, but as they cannot be obtained so readily in an anhydrous condition, the reaction does not proceed so cleanly, and the products are not easily purified.

Throughout these experiments we have employed the nitrogen chloride and bromide derived from 2 : 4-dichloroacetanilide, both of which are prepared in quantity without any difficulty. Further, 2 : 4-dichloroacetanilide, which is always regenerated in the reaction, is only slightly soluble in cold chloroform, whilst the other product or products are very soluble.

The first reaction of an amine with a nitrogen chloride or bromide is represented by the equation (where X = Cl or Br):

$$Ph{\cdot}NXAc + R{\cdot}NH_2 = R{\cdot}NHX + Ph{\cdot}NHAc.$$

In the case of the aliphatic amines, the chloroamines can be isolated. The bromoamines, however, decompose so readily that we have not been able to isolate them.

With all anilines, further reactions follow. Either the halogen wanders into the nucleus and takes up ortho- and para-positions relatively to the NH_2 group, or azobenzenes are formed with elimination of hydrogen chloride or hydrogen bromide. The latter reaction only plays a subordinate part, except when positions 2, 4, and 6 in the nucleus are occupied, and wandering of the halogen cannot therefore take place.

When 1 mol. of a nitrogen chloride or bromide interacts with 1 mol. of an aniline, it is found that the monohalogen derivative is almost exclusively formed. Thus aniline yields only *o*- and *p*-monochloroanilines and no 2 : 4-dichloroaniline, whilst *p*-chloroaniline yields only 2 : 4-dichloroaniline and no 2 : 4 : 6-trichloroaniline. When more than one aniline is present, the nitrogen halogen derivative always reacts preferentially with the least substituted base. In one

experiment, 1 mol. of the nitrogen chloride, dissolved in chloroform, was added to a chloroform solution containing 1 mol. of *p*-chloroaniline, and 1 mol. of 2 : 4-dichloroaniline. Only a trace of *s*-trichloroaniline was recognisable in the product, while no unchanged *p*-chloroaniline was discovered.

As weighed quantities of the pure substituted nitrogen chlorides can be used, this reaction affords a very simple means of introducing one atomic proportion of chlorine into an aniline. The yields are nearly quantitative and the products readily isolated in a pure state. It provides also a convenient method of chlorinating anilines already substituted in both the 2- and 4-positions. As is well known, the chlorination of anilides only leads to the entrance of chlorine into the para- and *one* ortho-position. Although, with anilines, chlorine itself can effect substitution in *both* ortho-positions, in many cases much oxidation of the aniline takes place, and the yield is consequently small.

With aniline and monomethylaniline, both the *o*- and *p*-monochloro-derivatives are formed. About equal proportions of each are obtained in the case of the former, a result which is noteworthy, as our previous observations have shown that in the transformation of acetylchloroaminobenzene, *p*-chloroacetanilide is the chief product, only some 5 per cent. of *o*-chloroacetanilide being produced (Trans., 1900, 77, 797).*

On the other hand, *p*-bromoaniline appears to be exclusively formed when aniline interacts with a nitrogen bromide.

Metasubstituted anilines also yield *o*- and *p*-chloro-derivatives, whilst from ortho-substituted anilines only 2 : 4-di-derivatives are produced.

The formation of azobenzenes from the first formed halogen-amino-compounds may be represented by the following equation :

$$2Ph{\cdot}NHX = Ph{\cdot}N{:}N{\cdot}Ph + 2HX.$$

The formation of azo-derivatives takes place best, at least in unsubstituted bases (for example, aniline and *o*- and *p*-toluidine), when excess of the base is used, as the acid then appears as a hydrochloride (or hydrobromide). Thus, in one experiment with aniline,

* In this connection may be mentioned the experiments of Loeb (*Ber.*, 1896, **29**, 1895) on the electrolysis of a hydrochloric acid solution of nitrobenzene. He found that *o*-chloroaniline was formed in large proportion together with the *p*-chloro-derivative.

Again it has been observed that the nature of the acyl group replacing the aminic hydrogen of aniline affects the proportion of the *o*- and *p*-derivatives formed on nitration. Thus Lellmann (*Annalen*, 1883, **221**, 6) found that benzanilide yielded more *o*-nitro-derivative than did acetanilide.

75 per cent. of the amine was converted into *o*- and *p*-chloroanilines, whilst as much as 25 per cent. appeared as azobenzene.*

With nitrogen bromides, on the other hand, these anilines yield very little azo-compound.

Anilines which are substituted in positions 2, 4, and 6, such as *s*-trichloroaniline and *s*-tribromoaniline, yield chloro- and bromo-amino-derivatives, which cannot undergo transformation, and especially readily form azo-compounds. The bromoamino-derivatives undergo this decomposition more readily than the chloroamino-derivatives.

Action of Acetylchloroamino- and Acetylbromoamino-2 : 4-dichlorobenzene on Amines.

Dibenzylamine.—Acetylchloroamino-2 : 4-dichlorobenzene (1 mol.), dissolved in a little dry chloroform, was added to dibenzylamine (1 mol.) dissolved in the same solvent. Little heat was developed. The dichloroacetanilide which separates was filtered off and the chloroform evaporated. The residue crystallised from petroleum (b. p. 50—80°) in large rhombs melting at 56°, and proved to be the dibenzylchloroamine, $(C_6H_5\cdot CH_2)_2NCl$, described by Berg (*Bull. Soc. Chim.*, 1893, [ii], **26**, 189).

0·2506 liberated I = 21·35 c.c. *N*/10 iodine. Cl as :NCl = 15·11.
$C_{14}H_{14}NCl$ requires Cl as :NCl = 15·33 per cent.

When acetylbromoamino-2 : 4-dichlorobenzene was employed, a similar reaction took place, but the dibenzylbromoamine formed was so unstable that it could not be isolated.

Other primary and secondary aliphatic amines gave similar results. For example, when an ethereal solution of the nitrogen chloride was added to an aqueous solution of methyl- or ethyl-amine, dichloroacetanilide immediately separated. On evaporating the ether, methyl- or ethyl-chloroamine was left as an oil, which was exceedingly irritating to the eyes, and set free iodine from potassium iodide.

Aniline.—A solution of the nitrogen chloride (12 grams or 1 mol.) in chloroform was gradually added to a cooled chloroform solution of

* It is very probable that the preparation of azobenzene and azotoluene by the action of *dry* bleaching powder on the respective bases in the presence of chloroform depends on the formation of the chloroamino-derivatives. Schmitt (*J. pr. Chem.*, 1878, **18**, 195; 1879, **19**, 314) found that the azobenzene produced represented one-third of the aniline. He does not account for the remaining two-thirds of the base, and does not seem to have anticipated the formation of chloroanilines. In the presence of water, no azo-compounds are formed, a fact which points to the action not being one of direct oxidation.

aniline (23 grams or 5 mols.). The reaction was accompanied by development of heat, and the solution became highly coloured. A mixture of dichloroacetanilide and aniline hydrochloride separated; the latter weighed 1·76 grams.

The chloroform mother liquor was partially evaporated, and petroleum added to precipitate the remainder of the anilide. The anilines were now extracted with hydrochloric acid. After evaporating the solvents, a residue of azobenzene remained, 1·14 grams being obtained instead of 1·23 grams which theoretically corresponds with the quantity (1·76 grams) of aniline hydrochloride.

In another experiment, in which 4 mols. of the nitrogen chloride to 5 mols. of aniline were used, the anilines were separated by fractionally distilling in steam from sulphuric acid. *o*- and *p*-Chloroanilines were obtained in nearly equal amounts.

Monomethylaniline.—The chloroamine and methylaniline dissolved in chloroform were mixed in molecular proportion. Much colour was developed in the reaction. The anilines were separated as in the previous experiment. The final fraction was acetylated and proved to be *Acetyl-4-chloromethylaniline.*—It crystallised from petroleum in pearly, white plates melting at 92°.

0·1935 gave 0·151 AgCl. Cl = 19·3.

$C_9H_{10}ONCl$ requires Cl = 19·31 per cent.

On hydrolysis, *p*-chloromethylaniline boiling at 240° was obtained. The latter was also prepared for comparison by heating methyl iodide with *p*-chloroaniline at 100° in a sealed tube and isolated in the usual manner through its nitroso-derivative.

o-*Chloromethylaniline* was contained in the first fraction from the distillation with steam. It was purified by distillation under reduced pressure, and boils at 95—96° under 12 mm., and at 218° under 760 mm. pressure. For comparison, this compound was synthesised from *o*-chloroaniline and methyl iodide.

0·2726 gave 0·2782 AgCl. Cl = 25·23.

C_7H_8NCl requires Cl = 25·04 per cent.

The quantity of *p*-chloromethylaniline formed in the reaction of a nitrogen chloride on methylaniline largely exceeds that of the *o*-chloro-derivative.

o-, m-, and p-*Toluidines.*—With each of these bases, considerable quantities of the corresponding azotoluene were formed. Thirty to forty per cent. of *p*-toluidine appeared as azo-compound. In addition, *o*-toluidine yielded 5-chloro-*o*-toluidine (melting at 30°); *m*-toluidine, 6-chloro-*m*-toluidine (melting at 83°); and *p*-toluidine, 3-chloro-*p*-

ine, the acetyl derivative of which melted at 118°.

Ortho-substituted Anilines.—*o*-Chloroaniline is almost entirely converted into 2 : 4-dichloroaniline, very little azo-compound being formed.

o-Nitroaniline yielded the 2-nitro-4-chloroaniline of Körner (*Jahresb.*, 1875, 351). It melted at 116—117°, and gave an acetyl derivative melting at 102°, which we have also obtained by the nitration of *p*-chloroacetanilide (Chattaway and Orton, *Ber.*, 1900, **33**, 3062).

Meta-substituted Anilines.—*m*-Bromoaniline yields a mixture of two chlorobromoanilines, which were separated by distilling in a current of steam from sulphuric acid. The larger portion, which distilled over first, was 2-chloro-5-bromoaniline melting at 45° (Clarke, *Amer. Chem. J.*, 1892, **14**, 561). Its acetyl derivative was sparingly soluble in 50 per cent. acetic acid, from which it separated in needles melting at 141°.

0·0977 gave 0·1317 AgCl + AgBr and 0·0457 Cl + Br. Cl = 14·68 ; Br = 32·09.

$C_8H_7ONClBr$ requires Cl = 14·26 ; Br = 32·17 per cent.

The smaller portion, which distilled over after complete neutralisation of the acid, was 3-bromo-4-chloroaniline melting at 78° (Wheeler and Valentine, *Amer. Chem. J.*, 1895, **17**, 697). Its acetyl derivative melts at 130°, and crystallises in rhombs fairly soluble in 50 per cent. acetic acid.

0·2649 gave 0·3558 AgCl + AgBr and 0·1238 Cl + Br. Cl = 14·39 ; Br = 32·35.

$C_8H_7ONClBr$ requires Cl = 14·26 ; Br = 32·17 per cent.

m-*Nitroaniline.*—3-Nitro-4-chloroaniline is the chief product, although other chloronitroanilines are formed. After evaporation of the chloroform, the residue was recrystallised from petroleum and then acetylated. The anilide was repeatedly crystallised from dilute alcohol, and then melted at 145°. This anilide has been prepared by us from 3-nitro-4-chloroaniline, obtained by nitration of *p*-chloroaniline (Chattaway and Orton, *loc. cit.*).

m-*Chloroaniline*, when treated with acetylbromoamino-2 : 4-dichlorobenzene, yielded 3-chloro-4-bromoaniline, melting at 67—68° (Wheeler and Valentine, *loc. cit.*).

Para-substituted Anilines.—*p*-Chloro-, *p*-bromo-, and *p*-nitro-anilines all readily yield monochloro-derivatives, in which chlorine is in the ortho-position relatively to the amino-group ; azo-compounds are formed only in small quantities.

2 : 4-*Disubstituted Anilines.*—These anilines react with chloro- and bromo-amino-compounds, with a smaller evolution of heat than do less substituted anilines, and the formation of azo-derivatives takes place only

to a slight extent. 2 : 4-Dichloroaniline yields 2 : 4 : 6-trichloroaniline; 2 : 4-dibromoaniline, 2 : 4-dibromo-6-chloroaniline; and 2-chloro-*p*-nitroaniline, 2 : 6-dichloro-*p*-nitroaniline.

s-Trisubstituted Anilines.—On mixing solutions of these anilines in chloroform with solutions of acetylchloro- or acetylbromo-amino-2 : 4-dichlorobenzene, crystals of dichloroacetanilide begin immediately to separate. No heat is developed in the reaction. The chloroamino-derivative of *s*-trichloroaniline can be obtained in an impure state, as a faintly coloured oil, on evaporation of the solvent. It soon becomes deep-red from decomposition into the azo-compound, a change which also takes place in the solution after a short time. The bromoamino-derivative decomposes still more readily.

2 : 4 : 6 : 2′ : 4′ : 6′-*Hexachloroazobenzene*, hitherto unknown, can thus be readily prepared from *s*-trichloroaniline. Chloroform solutions of acetylbromoamino-2 : 4-dichlorobenzene and trichloroaniline are mixed; after separation of the anilide, the filtered solution is evaporated, and the residue recrystallised from a mixture of alcohol and chloroform. The azo-compound separates in fine, dark red needles melting at 188°, insoluble in alcohol, but very soluble in chloroform or benzene.

0·147 gave 0·326 AgCl. Cl = 54·83.

$C_{12}H_4N_2Cl_6$ requires Cl = 54·7 per cent.

It is reduced by tin and hydrochloric acid to trichloroaniline.

Tribromoaniline, on similar treatment, gave hexabromoazobenzene melting at 213° (Pechmann and Nold, *Ber.*, 1898, **31**, 564).

The Action of Nitrogen Halogen Compounds on Phenylhydrazine.

All chloro-, bromo-, and iodo-amines interact very readily with phenylhydrazine. Two reactions take place, according as the nitrogen halogen compound or the hydrazine is in excess. Thus when phenylhydrazine is added to an excess of acetylchloroamino-2 : 4-dichlorobenzene, nitrogen, chlorine, chlorobenzene, and the regenerated anilide are formed. The final result is represented by the equation:

$$C_6H_5\cdot NH\cdot NH_2 + 3C_6H_3Cl_2\cdot NClAc = C_6H_5Cl + N_2 + Cl_2 + 3C_6H_3Cl_2\cdot NHAc.$$

In this reaction, much heat is developed. When excess of the hydrazine is present, the final result of the reaction (which is not accompanied by much development of heat) is represented thus:

$$4C_6H_5\cdot NH\cdot NH_2 + 2C_6H_3Cl_2\cdot NClAc = C_6H_5N_3 + C_6H_5\cdot NH_2 + 2C_6H_3Cl_2\cdot NHAc + 2C_6H_5\cdot NH\cdot NH_2,HCl.$$

A hydrazino-halogen compound is probably the first product,

which then decomposes into azimidobenzene, aniline, and hydrogen chloride.*

$$2C_6H_5\cdot NH\cdot NHCl = C_6H_5N_3 + C_6H_5\cdot NH_2 + 2HCl.$$

Nitrogen iodide reacts with phenylhydrazine in a similar manner; and as in this case it is impossible to exclude water, the presence of the latter does not modify the course of the reaction.

(1) Action of acetylchloroamino-2 : 4-dichlorobenzene on excess of phenylhydrazine.

A solution of the nitrogen chloride dissolved in chloroform was slowly run into chloroform containing a large excess of phenylhydrazine. The hydrochloride of the base immediately separated together with the anilide. After filtration, the mother liquor was repeatedly extracted with dilute hydrochloric acid, and then evaporated. The oil which remained was purified by distillation in steam. It was insoluble in hydrochloric acid, and contained no halogen. On treating a solution in chloroform with excess of bromine, fine needles of 2:4:6-tribromoaniline hydrobromide separated. The liquid is therefore azimidobenzene.

The hydrochloric acid extracts were evaporated to a small bulk, and after filtering off the phenylhydrazine hydrochloride, the mother liquor was made alkaline and distilled in steam. The oil which distilled over proved to be aniline, and yielded acetanilide on treatment with acetic anhydride.

In one experiment, in which 16 grams of acetylchloroamino-2 : 4-dichlorobenzene were used, 13·11 grams of 2 : 4-dichloroacetanilide, 2·24 grams of hydrogen chloride, 3·12 grams of aniline, and 2 grams of azimidobenzene were obtained, whilst 13·69, 2·34, 2·75, and 4·02 grams respectively are required by the equation. The low yield of the azimidobenzene is undoubtedly due to some loss in the evaporation of the large quantity of chloroform.

(2) Action of phenylhydrazine on excess of acetylchloroamino-2 : 4-dichlorobenzene.

The solution of phenylhydrazine in chloroform was slowly added to the solution of the nitrogen chloride. Heat was developed, and much gas given off. After removal of the anilide by filtration, and evaporation of the chloroform, the residual oil was distilled in steam. It proved to be chlorobenzene, boiling at 132°.

* Fischer (*Annalen*, 1877, **190**, 67) found that iodine has two reactions with phenylhydrazine, according as one or the other substance is in excess. With the halogen n excess. iodobenzene, nitrogen and hydriodic acid are produced, and with hydrazine in excess azimidobenzene, aniline, and phenylhydrazine hydriodide. As we find that these reactions can take place equally well in the absence of water, it is very probable that this action is not a simple oxidation, as Fischer suggests, but depends on the formation of an iodohydrazine.

(3) Action of nitrogen iodide ($NH_3 \cdot NI_3$) on phenylhydrazine.

In this case, as it was impossible to dry the nitrogen iodide, the latter was added to an aqueous emulsion of phenylhydrazine. The reaction takes place very readily and in the presence of excess of phenylhydrazine without marked development of heat. Azimidobenzene, aniline, and hydriodic acid (as phenylhydrazine hydriodide) were formed.

(4) Action of iodine on phenylhydrazine in anhydrous solution.

With excess of phenylhydrazine, little heat was developed. After removal of the hydriodide of the base by filtration, the solution was thoroughly extracted with hydrochloric acid. On evaporation of the chloroform, azimidobenzene was left. The acid extract contained aniline, together with the excess of phenylhydrazine.

CHEMICAL LABORATORY,
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L.—*The Preparation of* o*-Chloroaniline.*

By F. D. CHATTAWAY and K. J. P. ORTON.

THE preparation and purification of this aniline have hitherto offered considerable difficulties, as both the substances from which it has been obtained, namely, *o*-chloronitrobenzene and *o*-nitroaniline, are not easily prepared.

From the product of the nitration of chlorobenzene, the *o*-chloronitrobenzene cannot practically be obtained free from the *p*-derivative and the commercial material, which is by no means cheap, invariably contains large quantities of the latter. After reduction, the *o*- and *p*-chloroanilines have to be separated.

o-Nitroaniline also is not easily prepared, for although it is formed in considerable quantity in the nitration of acetanilide (or benzanilide), it is difficult to separate the *pure* ortho- from the para-compound. In addition, the subsequent conversion into *o*-chloroaniline is a wasteful process.

The authors have recently observed (Trans., 1900, 77, 797) that in the transformation of acetylchloroaminobenzene, *o*-chloroacetanilide is formed together with the *p*-chloro-derivative. Although the proportion of the ortho-compound is only small (5 to 8 per cent.), this method is found to be convenient for preparing *o*-chloroaniline.

One part of acetanilide is dissolved in 3 to 4 parts of glacial acetic acid, and the *calculated* quantity of a strong solution of bleaching powder (0·5 to 0·7 *N*) is gradually added.* Considerable heat is

* A solution of bleaching powder, about 0·7 *N*, can be obtained by allowing water to stand over excess of the solid for several hours.

developed, but no cooling is necessary. Crystals begin to separate as soon as the bleaching powder is added. After standing for some hours to allow of complete transformation of the chloroamino-derivative first formed, the crystalline mass, which consists of a mixture of *o*- and *p*-chloroacetanilide, is filtered off, and, together with any further quantity which separates from the mother liquor on dilution, dissolved in boiling alcohol. On cooling, *p*-chloroacetanilide separates in a nearly pure state. The alcoholic mother liquor is evaporated to half its volume, when a further quantity of the *p*-chloro-compound crystallises out. To the mother liquor is then added concentrated sulphuric acid (10 parts of acid for every 100 parts of acetanilide), and the mixture boiled under a reflux apparatus for 1½ hours in order to hydrolyse the anilides. On distilling the *acid* product in steam, *o*-chloroaniline comes over, now mixed with only a small amount of the para-derivative. To the oil suspended in water is added an equal weight of sulphuric acid, the mixture afterwards being distilled in steam. In order to effect the final purification of the *o*-chloroaniline, the distillate is acetylated by warming for a short time with excess of acetic anhydride. After removing the excess of anhydride by evaporation, the anilide is recrystallised by boiling it with a considerable quantity of petroleum (b. p. 80—100°), and adding benzene in small quantities until it is all or nearly all dissolved. On cooling, pure *o*-chloroacetanilide crystallises out in needles, and the yield amounts to about 50 grams from a kilogram of acetanilide.

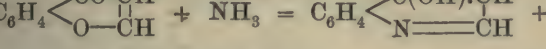
CHEMICAL LABORATORY,
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LI.—*Condensation of Phenols with Esters of the Acetylene Series. Part IV. Benzo-γ-pyrone and its Homologues.*

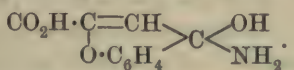
By SIEGFRIED RUHEMANN and HAROLD W. BAUSOR, B.A.

RUHEMANN and STAPLETON (Trans., 1900, **77**, 1184) have shown that phenoxyfumaric acid, under the influence of concentrated sulphuric acid, loses water and condenses to benzo-γ-pyronemonocarboxylic acid which, on distillation, loses carbon dioxide and yields benzo-γ-pyrone. We have applied this reaction to the cresoxyfumaric acids and thus obtained the isomeric toluo-γ-pyrones which are described in this paper. Benzo-γ-pyrone and its methyl derivatives dissolve in alcohol and ether as well as in boiling water, and their solutions in concentrated sulphuric acid show a blue fluorescence; they also possess an aromatic odour which is especially apparent on heating them with water.

Our attempts to transform benzo-γ-pyrone and its homologues into hydroxyquinolines according to the equation



have as yet been unsuccessful, since, at the ordinary temperature, they seem to form additive compounds with ammonia, which, however, on heating readily dissociate into their components. From benzo-γ-pyronecarboxylic acid, an additive product of this kind has been obtained which most probably has the formula



On boiling this substance with water, however, it loses ammonia, as also does the compound obtained by the action of aqueous ammonia on ethyl benzo-γ-pyronecarboxylate. By acting on the ester with alcoholic ammonia, an additive compound does not seem to be formed, or, if so, only to a small extent, and in its stead the amide of benzo-γ-pyronecarboxylic acid is obtained. When heated with alcoholic or aqueous ammonia at 160°, benzo-γ-pyrone and its homologues suffer decomposition.

Experimental.

Benzo-γ-pyronecarboxylic Acid.

When analysed previously (Ruhemann and Stapleton, *loc. cit.*), the silver salt seemed to contain one molecular proportion of water; we now find that this result was due to impurity, as the pure salt, obtained by crystallisation, is anhydrous. On analysis:

0·2217 left on ignition 0·0804 Ag. Ag = 36·27.

$C_{10}H_5O_4Ag$ requires Ag = 36·36 per cent.

Benzo-γ-pyronecarboxylic acid dissolves in concentrated aqueous ammonia, forming a yellow solution. After standing overnight, this is freed from ammonia by heating it under diminished pressure; on slightly acidifying the solution with dilute hydrochloric acid, a yellowish solid is precipitated which, after washing with water, is dried in a vacuum over sulphuric acid. On analysis:

0·2799 gave 15·5 c.c. moist nitrogen at 17° and 752 mm. N = 6·35.

$C_{10}H_9O_4N$ requires N = 6·76 per cent.

As already pointed out above, this result indicates that the compound is an additive product of ammonia with benzo-γ-pyronecarboxylic acid. This view is supported by the facts that the yellowish solution of the substance in alcohol becomes colourless and evolves ammonia on boiling, and that the solution on cooling deposits colourless

needles which melt and decompose at 251° and are identical with benzo-γ-pyronecarboxylic acid.

The behaviour of the acid towards ammonia is similar to that of its ester.

Ethyl Benzo-γ-pyronecarboxylate, $CO_2C_2H_5\cdot C(O\cdot C_6H_4)=CH>CO$, is obtained by boiling the solution of the acid in absolute alcohol with a few c.c. of concentrated sulphuric acid for six hours on the water-bath. After mixing the cold solution with water, it is shaken with ether and the ethereal layer freed from unchanged acid by sodium carbonate. On evaporating the ether, a solid remains which crystallises from dilute alcohol in long, colourless, silky needles melting at 69—70°. On analysis:

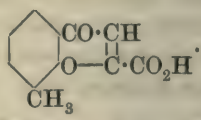
0·1907 gave 0·4615 CO_2 and 0·0819 H_2O. C = 66·00; H = 4·77.
$C_{12}H_{10}O_4$ requires C = 66·06; H = 4·59 per cent.

Amide of Benzo-γ-pyronecarboxylic Acid, $NH_2\cdot CO\cdot C(O\cdot C_6H_4)=CH>CO$.—Ethyl benzo-γ-pyronecarboxylate dissolves in alcoholic ammonia, and, after a few minutes, the yellowish solution deposits an almost colourless solid which increases in quantity on standing overnight. This dissolves only sparingly in water or alcohol, and crystallises from the hot solutions in slightly yellow prisms which soften at about 230° and melt to a dark liquid at 252°. On analysis:

0·2122 gave 14·2 c.c. moist nitrogen at 19° and 744 mm. N = 7·52.
$C_{10}H_7O_3N$ requires N = 7·41 per cent.

The formation of the amide seems to be preceded by that of its additive compound with ammonia; the latter, however, is unstable, and if the ester remains in contact with an aqueous instead of with an alcoholic solution of ammonia, a yellow product is obtained which, on boiling with water, loses ammonia and yields the amide.

o-Toluo-γ-pyronecarboxylic Acid,



This acid is prepared in the same manner as benzo-γ-pyronecarboxylic acid, namely, by dissolving *o*-cresoxyfumaric acid (Ruhemann and Beddow, Trans., 1900, 77, 1124) in concentrated sulphuric acid, allowing the solution to stand for a day, and then gradually adding it to ice-cold water. The white solid which is thus precipitated crystallises from rectified spirit in silky needles which melt and decompose at 255—256°. On analysis:

0·1769 gave 0·4192 CO_2 and 0·0630 H_2O. C = 64·63 ; H = 3·96.
$C_{11}H_8O_4$ requires C = 64·71 ; H = 3·92 per cent.

The silver salt obtained as a white precipitate on mixing a solution of the acid in ammonia with silver nitrate, dissolves with difficulty in boiling water, and on cooling crystallises in colourless needles. On analysis :

0·2815 left, on ignition, 0·0977 Ag. Ag = 34·71.
$C_{11}H_7O_4Ag$ requires Ag = 34·73 per cent.

o-Toluo-γ-pyrone, $CH_3 \cdot C_6H_3 \langle \begin{matrix} CO \cdot CH \\ O — CH \end{matrix}$.

o-Toluo-γ-pyronecarboxylic acid, when heated above its melting point, loses carbon dioxide, and an oil distils over which soon sets to a solid. This dissolves in light petroleum (b. p. 70—80°), leaving behind a small quantity of unaltered *o*-toluo-γ-pyronecarboxylic acid. From the solution on cooling, colourless needles of *o*-toluo-γ-pyrone separate which melt at 84—85°. On analysis :

0·1868 gave 0·5135 CO_2 and 0·0838 H_2O. C = 74·97 ; H = 4·98.
$C_{10}H_8O_2$ requires C = 75·00 ; H = 5·00 per cent.

o-Toluo-γ-pyrone dissolves with the greatest ease in alcohol, but less readily in hot water ; it has an aromatic odour, which is especially noticeable on boiling the aqueous solution. The solution of *o*-toluo-γ-pyrone in concentrated sulphuric acid shows a fluorescence similar to that of its lower homologue.

m-*Toluo-γ-pyronecarboxylic Acid*, *m*-$CH_3 \cdot C_6H_3 \langle \begin{matrix} CO \cdot CH \\ O — C \cdot CO_2H \end{matrix}$.

m-Cresoxyfumaric acid (Ruhemann and Beddow, Trans., 1900, **77**, 1124), on treatment with concentrated sulphuric acid, as in the former cases, loses water and condenses to the pyrone compound. This crystallises from dilute alcohol in colourless plates which soften at about 222° and melt at 233—234° with decomposition. On analysis :

0·1775 gave 0·4204 CO_2 and 0·0655 H_2O. C = 64·59 ; H = 4·10.
$C_{11}H_8O_4$ requires C = 64·71 ; H = 3·92 per cent.

m-Toluo-γ-pyrone, $CH_3 \cdot C_6H_3 \langle \begin{matrix} CO \cdot CH \\ O — CH \end{matrix}$.

This compound is obtained by heating the acid, and distils at about 280° as a yellowish oil which, on cooling, solidifies. It is readily soluble in alcohol, ether, chloroform, or light petroleum, but only

sparingly so in boiling water, and crystallises from the aqueous solution in colourless needles melting at 72—73°. On analysis :

0·1696 gave 0·4653 CO_2 and 0·0788 H_2O. C = 74·82 ; H = 5·16.
$C_{10}H_8O_2$ requires C = 75·00 ; H = 5·00 per cent.

m-Toluo-γ-pyrone also has a pleasant, aromatic odour, and its solution in concentrated sulphuric acid shows a faint blue fluorescence.

p-*Toluo-γ-pyronecarboxylic Acid*, $p\text{-}CH_3\cdot C_6H_3<\begin{matrix}CO\cdot CH\\ \|\\ O—C\cdot CO_2H\end{matrix}$.

p-*Cresoxyfumaric acid*, $CO_2H\cdot C(O\cdot C_6H_4\cdot CH_3p):CH\cdot CO_2H$, which is required for the preparation of the above acid, has not been recorded before. We have obtained it by the hydrolysis of ethyl *p*-cresoxyfumarate (Ruhemann and Beddow, Trans., 1900, 77, 1125) with alcoholic potash. It forms yellowish plates which dissolve in boiling water and melt with decomposition at 197°. On analysis :

0·1948 gave 0·4250 CO_2 and 0·0784 H_2O. C = 59·50 ; H = 4·47.
$C_{11}H_{10}O_5$ requires C = 59·46 ; H = 4·50 per cent.

This acid readily dissolves in cold concentrated sulphuric acid ; after standing overnight, the dark solution is added to ice-cold water, when *p*-toluo-γ-pyronecarboxylic acid is precipitated as a white solid which crystallises from dilute alcohol in colourless needles and melts and decomposes at 258°. On analysis :

0·1939 gave 0·4594 CO_2 and 0·0631 H_2O. C = 64·62 ; H = 3·62.
0·1747 „ 0·4164 CO_2 „ 0·0614 H_2O. C = 65·00 ; H = 3·90.
$C_{11}H_8O_4$ requires C = 64·71 ; H = 3·92 per cent.

p-*Toluo-γ-pyrone*, $CH_3\cdot C_6H_3<\begin{matrix}CO\cdot CH\\ \|\\ O—CH\end{matrix}$.

This compound, formed on heating *p*-toluo-γ-pyronecarboxylic acid, crystallises from boiling water in colourless needles melting at 88—89°. On analysis :

0·1823 gave 0·5005 CO_2 and 0·0838 H_2O. C = 74·88 ; H = 5·11.
$C_{10}H_8O_2$ requires C = 75·00 ; H = 5·00 per cent.

p-Toluo-γ-pyrone is odourless, but on boiling its aqueous solution a pleasant aromatic odour is developed. The substance is readily soluble in alcohol or light petroleum, and its solution in concentrated sulphuric acid shows a blue fluorescence.

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CAMBRIDGE.

LII.—*Optical Activity of Certain Ethers and Esters.*

By Professor Philippe A. Guye.

In a recent publication, Messrs. John McCrae and T. S. Patterson (Trans., 1900, 77, 1096) have directed attention to the very interesting properties of the acetyl and phenacetyl derivatives of diethyl *d*-tartrate, and have shown that, according to their own observations and others made in Professor Frankland's laboratory, the phenacetyl group, which has a mass approximately equal to that of the toluyl group, nevertheless influences the rotatory power in a way which connects the phenacetyl group more closely with the acetyl group, or even the chloracetyl group, than with the toluyl group. In support of this conclusion, Messrs. McCrae and Patterson only quote Tschugaeff's previous observations (*Ber.*, 1898, 31, 360, 1778). As various researches prosecuted in my laboratory confirm Messrs. McCrae and Patterson's conclusions (Guye and Chavanne, *Bull. Soc. Chim.*, 1896, [iii], 15, 177; *Arch. Sci. phys. nat. Genève*, 1896, [iii], 1, 34, 121; Welt, *Ann. Chim. Phys.*, 1895, [vii], 7, 142; Guye and Babel, *Arch. Sci. phys. nat. Genève*, 1899, [iii], 7, 23, 109), it appears to me advisable to give, in the following table, a *résumé* of the specific rotatory powers, $[\alpha]_D$, of these substances at the ordinary temperature (about 15° to 20°).

All the substances mentioned in this table are amyl derivatives, obtained by help of Claudon's primary active alcohol, having a specific rotatory power of $[\alpha]_D$ $-4{\cdot}4°$ to $-4{\cdot}5°$. They may be divided into two groups:

(1) Mixed amyl ethers of the formula $C_5H_{11}{\cdot}O{\cdot}R$, in which R represents the radicles, phenyl, C_6H_5, and *o*-, *m*-, or *p*-tolyl, C_7H_7.

(2) Amyl esters of the formula $R{\cdot}CO{\cdot}O{\cdot}C_5H_{11}$, in which R represents phenyl (of benzoic acid), *o*-, *m*-, or *p*-toluyl (of toluic acid), benzyl (of phenylacetic acid), or phenylethenyl (of phenylpropionic acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$).

Substances.	$[\alpha]_D$.	Authors.
First Group:		
Phenyl amyl ether.....	$+4{\cdot}0°$	Welt.
Benzyl ,, ,, ...	1·82	Guye and Chavanne.
o-Tolyl ,, ,, ...	3·9	Welt.
m-Tolyl ,, ,, ...	3·9	,,
p-Tolyl ,, ,, ...	4·3	,,
n-Butyl ,, ,, ...	1·33	Guye and Chavanne.

Substances.	$[\alpha]_D$.	Authors.
Second Group:		
Amyl benzoate	4·96°	Guye and Chavanne.
„ *o*-toluate	4·55	„ „
„ *m*-toluate	5·05	„ „
„ *p*-toluate	5·20	„ „
„ phenylacetate	3·84	„ „
„ phenylpropionate...	2·15	„ „
„ propionate	2·77	„ „
„ monochloracetate...	3·44	„ „

In order to show the analogy which exists between the rotatory power of substances containing the benzyl group, $C_6H_5 \cdot CH_2$, and compounds of the fatty series, data relating to *n*-butyl amyl ether have been inserted in the first group, and those relating to amyl propionate and amyl monochloracetate in the second. In this connection, it may be mentioned that *n*-butyl amyl ether and amyl propionate give the highest values for $[\alpha]_D$ among the homologous series of mixed amyl ethers, and among those of the amyl esters derived from fatty acids.

From the above figures, it appears that the benzyl radicle resembles the alkyl groups, C_nH_{2n+1}, rather than the phenyl, C_6H_5, and toluyl, C_7H_7, groups in the influence it exerts on rotatory power; this confirms the statements of Professor Frankland and his pupils.

It must be remarked, however, that this conclusion is only one case of the much more general statement already made in a recent paper (Guye and Babel, *loc. cit.*, p. 114; see also Tschugaeff, *loc. cit.*), namely, that when *substitutions of chains or groups of elements are effected in an asymmetric carbon compound in positions sufficiently far removed from the asymmetric carbon atom, the rotatory power is only slightly affected.*

This fact is clearly shown from the rotatory powers of benzoate, phenylacetate, and phenylpropionate of amyl. It is also to be noticed that the analogy existing between the rotatory powers of benzyl and acetyl derivatives is even more striking in the case of the compounds mentioned in the table than in that of the esters of tartaric acid studied by McCrae and Patterson. This is due to the fact that inasmuch as the latter contained two asymmetric carbon atoms, it is impossible to carry out a substitution which does not influence both of these atoms, and thus alter their optical powers algebraically; this may result in a specific rotation $[\alpha]_D$ in which the influence of the substitution may be hidden by the algebraic superposition of the optical powers of two asymmetric carbon atoms. It is sufficient to note that this point has already been treated of in detail in a previous publication (Guye and Babel, *loc. cit.*, p. 109, *et seq.*).

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LIII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part II. Influence of* iso*Butyl Alcohol and of* sec.*Octyl Alcohol (Methylhexylcarbinol) on Ethyl Tartrate.*

By T. S. Patterson.

In a former paper (this vol., p. 167), the influence of water, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, and glycerol as solvents on the rotation of ethyl tartrate has been described. It was shown there that in the first four of these liquids the rotation of the dissolved ethyl tartrate diminishes as the molecular weight of the solvent increases, whilst the rotation in very dilute glycerol solutions lies between the values found in methyl and ethyl alcohols. Molecular weight determinations which had been carried out in connection with the rotation experiments appeared to lend no support to the idea that variation of rotation in solution is due to varying degree of association of the molecules of dissolved substance, and consequently an attempt was made to find some other cause for the phenomena observed. It was shown that the assumption of a connection between the internal pressure of the solvent as measured by its heat of disgregation and the specific rotation of the substance dissolved in it is in accordance with fact, provided that change of volume of an optically active molecule be admitted as likely to cause change of its asymmetry and consequently also of its rotation, it having been found that as the internal pressure decreases in passing from one solvent to another, the volume of the ethyl tartrate increases, whilst its rotation diminishes.

It appeared, however, that although the rotation in dilute *n*-propyl alcoholic solution becomes less than that of the free ester, the molecular-solution-volume remains somewhat smaller than the molecular volume, instead of attaining to a greater value as might be expected; it is therefore advisable, before undertaking the investigation of other classes of solvents, to ascertain how far the behaviour of the higher alcohols conforms to that which would be anticipated from the results of the former research, in regard not only to the connection between molecular-solution-volume and rotation, but also to another interesting point as well, namely, the existence of concentrations of minimum rotation.

The general appearance of the curves already obtained makes it probable that the latter phenomenon will be more marked in alcohols higher in the series than *n*-propyl, and consequently the previous research is extended in the present paper to include *iso*butyl and *sec*-octyl alcohols and the data thus obtained should illustrate sufficiently,

in the meantime at least, the general behaviour of this series of solvents.

The method of carrying out the experiments has already been fully described (*loc. cit.*, pp. 169—171), and it need perhaps only be remarked here that the rotation of the ethyl tartrate used was generally a little higher than that of the specimen the data for which are given on page 198 of the former communication. The ester used in the following experiments had an observed rotation of $+9{\cdot}35°$ instead of $+9{\cdot}244°$ in a 100 mm. tube at 20°, whence $[\alpha]_D^{20°}$ $+7{\cdot}76°$. This slightly higher rotation, however, does not affect comparison of these results with the previous ones.

Ethyl Tartrate in iso*Butyl Alcohol.*

Solutions containing 5, 9·996, 25, 50·005, 62·84, and 75·03 per cent. of ethyl tartrate were examined in the polarimeter at different temperatures. The numerical results obtained, along with other data relative to these experiments, will be found at the end of the paper (pp. 487—490), and are represented graphically by the curves in Fig. 1 (p. 479).

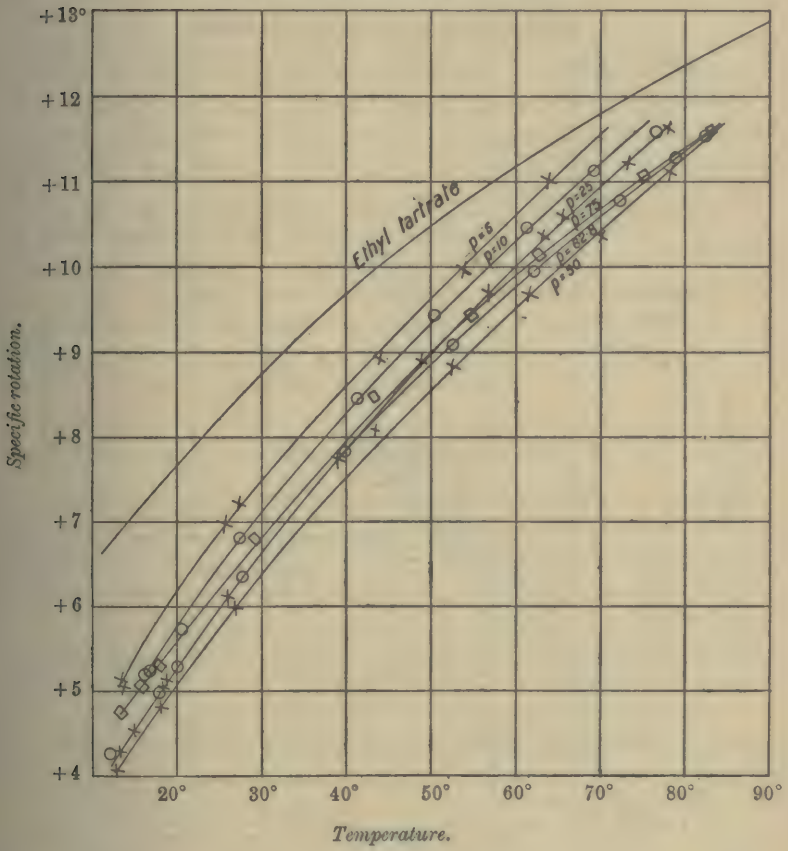
The results obtained are similar to those already recorded for ethyl tartrate in *n*-propyl alcohol, but in the present case the depression of rotation due to the action of the *iso*butyl alcohol is greater, so that none of these solutions has a rotation higher than that of the pure ester, within the limits of temperature of the experiments. At 20°, addition of alcohol to make a solution of $p=75$ diminishes the specific rotation by 2°; addition of more alcohol to make $p=62{\cdot}8$ is attended by a further depression of rotation of 0·3°, whilst in 50 per cent. solution the lowest rotation observed is reached at 2·6° below that of the pure ester. Further dilution causes increase of rotation, a 25 per cent. solution having the same specific rotation as one of $p=62{\cdot}8$ at 20°, whilst that of a 10 per cent. solution lies 1·9°, and that of a $p=5$ solution 1·45° below that of ethyl tartrate. By plotting the values of the specific rotations of these solutions at 20° relative to concentration (grams of substance per 100 grams of solution), the curve marked "*iso*butyl alcohol" in Fig. 3 is obtained, from which it appears that at infinite dilution the specific rotation would be about $+6{\cdot}53°$, or 1·23° less than that of the free ester.

It is obvious that in this case, as in others to which attention has already been drawn, namely, *n*-propyl alcohol and glycerol, we have for any particular temperature a concentration of minimum rotation which for 20° lies at about $p=45$, moving as the temperature rises to a somewhat greater concentration.

It is of interest also to notice the gradual change in form of the

curves in Fig 1. That for a 75 per cent. solution has much the same form as that for the free ester, but it will be seen that the increase of rotation in the former, with increase of temperature, is somewhat greater than in the latter. This becomes more marked as the dilution increases, the sensitiveness to temperature of a $p=5$ solution being

FIG. 1.—*Ethyl tartrate in isobutyl alcohol.*

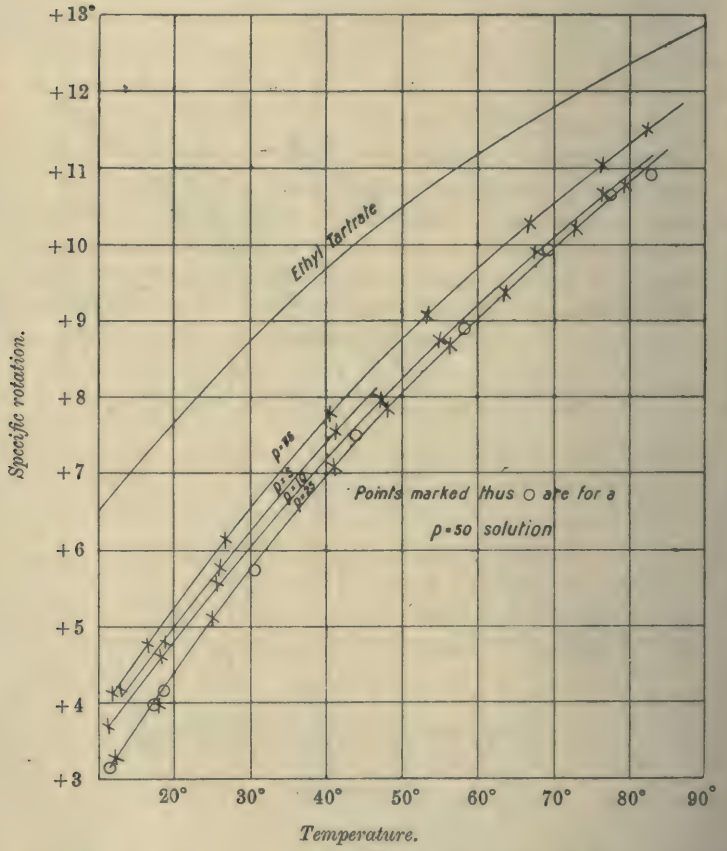


distinctly greater than that of ethyl tartrate itself. At higher temperatures in solution, therefore, the active molecule appears to be freed from some influence which in the homogeneous ester exercises a retarding effect on the increase of rotation with increase of temperature.

Ethyl Tartrate in sec.*Octyl Alcohol* (*Methylhexylcarbinol*).

As the octyl alcohol used in these experiments was found to be slightly active,* a small correction had to be introduced in calculating the value of the specific rotation of the ethyl tartrate dissolved in it, and the results thus obtained are probably free from any appreciable

FIG. 2.—*Ethyl tartrate in* sec.*octyl alcohol.*



error due to the action of the ethyl tartrate in modifying the rotation of the alcohol. The data obtained in the examination of 5, 10, 24·997,

* Marckwald and McKenzie in a recent paper (*Ber.*, 1901, **34**, 474) also point out that commercial octyl alcohol is optically active. They found α_D $-8'$ and $-10'$ ($l=2$), whereas from the figures on p. 491 of this paper, the alcohol used in the present investigation had the rotation $\alpha_D^{15°6°}$ $-16·5$ ($l=4$), so that the two values agree closely.

50·02, and 75·01 per cent. solutions will be found on pp. 491—493, and are also represented graphically in Fig. 2 (p. 480), where the curves show clearly the influence of temperature in varying the specific rotation of the different mixtures.

It is apparent that here again solution brings about diminution of rotation. At 20°, the rotations of these solutions lie respectively 2·75°, 2·93°, 3·4°, 3·4°, and 2·5° below that of pure ethyl tartrate, so that the effect of octyl alcohol in diminishing the rotation of this particular active substance is greater than that of *iso*butyl alcohol or of any other of the compounds previously examined. By plotting the values of the specific rotations of these solutions relatively to concentration, the curve marked "octyl alcohol" in Fig. 3 has been obtained, from which it is evident that in this case also we meet with a good example of a solvent whose maximum influence is exerted, not when it might be expected, at great dilution, but at a fairly high concentration. In this case, the minimum rotation occurs when $p = 39$, its value being $+4·28°$, or 3·48° less than that of pure ethyl tartrate at the same temperature. By extrapolation from this curve, the value of the specific rotation at infinite dilution is found to be $+5·24°$, or 2·52° lower than that of the free active substance.

Discussion of Results.

From the experiments detailed above, it appears that the influence of *iso*butyl alcohol and octyl alcohol is, so far as the rotation of ethyl tartrate is concerned, what might have been expected from the results communicated in the previous paper: the rotation continues to diminish with increase in molecular weight of the solvent. How much further this behaviour would be continued in the higher members of the same series cannot, of course, be stated, and in the meantime it does not seem to be of the first importance to decide the question. That the diminution of rotation does not depend merely on molecular weight is shown by the position which glycerol occupies with regard to the other solvents used. Although its molecular weight is greater than that of propyl alcohol, the specific rotation of dilute solutions of ethyl tartrate in it is higher than for similar solutions, not only in *n*-propyl alcohol but in ethyl alcohol as well.

In the former paper it has been shown that for the five solvents dealt with a qualitative agreement exists between specific rotation and molecular-solution-volume, even when water and glycerol are considered, although, on account presumably of their somewhat different chemical nature, their behaviour does not conform completely to that of the three primary alcohols. The important point, therefore, with which this communication is concerned is whether the

relationship just mentioned can be shown to exist also for the two new solvents. The molecular-solution-volume in them has therefore been calculated by means of the formula already used (this vol., pp. 189—190), and following are the results:

Molecular-solution-volume of ethyl tartrate.

$M=206$. *Molecular volume of ethyl tartrate* at 20° = 206/1·2053 = 170·9; $[\alpha]_D^{20°} = 7·76°$.

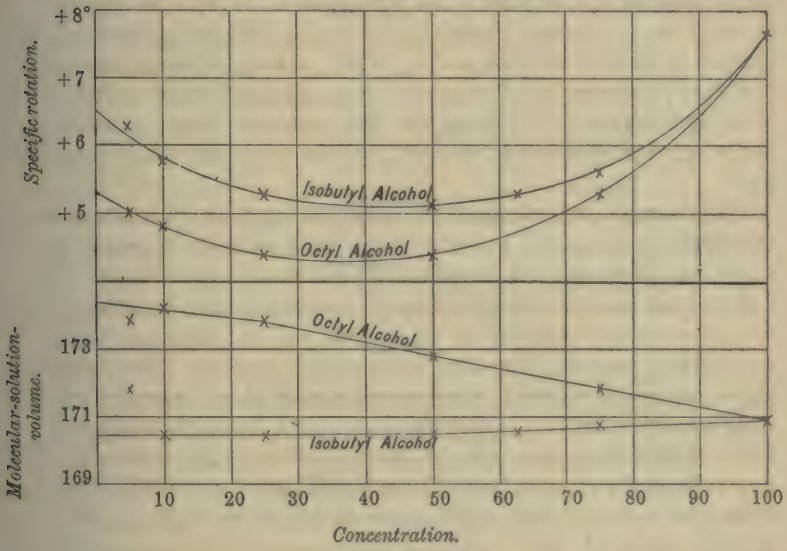
t.	*p.*	*d.*	δ.	M.S.V.	$[\alpha]_D^t$.
*iso*Butyl alcohol:					
20°	5·0005	0·8163	0·8029	171·80*	+6·20°
,,	9·995	0·8308	,,	170·44	5·76
,,	25	0·8764	,,	170·40	5·28
,,	50·005	0·9647	,,	170·54	5·11
,,	62·84	1·0174	,,	170·55	5·28
,,	75·03	1·0720	,,	170·74	5·60
sec. Octyl alcohol:					
20°	5·001	0·8326	0·8198	173·84	5·01
,,	10	0·8458	,,	174·27	4·82
,,	24·997	0·88825	,,	173·82	4·37
,,	50·02	0·9717	,,	172·80	4·37
,,	75·01	1·0748	,,	171·81	5·26

These figures are plotted in Fig. 3 (p. 483) relatively to percentage composition of solution and below the corresponding concentration-rotation curves, so that the behaviour of the ethyl tartrate with regard to rotational and volume change may be easily compared. The first figure given in the table for a $p=5$ solution in *iso*butyl alcohol—marked with an asterisk—is much too high, owing to a slight error in the density determination, which in the calculation of molecular-solution-volume becomes greatly magnified, but since the other experimental points sufficiently indicate the behaviour of the solutions, it was considered unnecessary to redetermine this number.

In the case of *iso*butyl alcohol, there is apparently little alteration in the volume of the dissolved ethyl tartrate as the concentration diminishes. By extrapolation, the volume at infinite dilution is found to be about 170·3 c.c., or only 0·6 c.c. less than that of ethyl tartrate in the homogeneous condition. Now if an intimate connection between rotation and volume actually exists, the specific rotation of

ethyl tartrate in this solvent ought to be almost identical with that of the free ester, on account of this similarity of volume. It is, however, less at infinite dilution by 1·23°, so that we do not meet here with any absolute agreement; in spite of this, however, the supposition that there is such a relationship is strengthened when the data regarding octyl alcohol are taken into account. In this case a considerably greater volume change—an increase—occurs on dilution, and this is very interesting, showing as it does that if there is a limiting value to which the molecular-solution-volume tends it is not that of the molecular-volume, and also that the dissolved active substance can have a greater volume in solution than in the free

FIG. 3.—*Relationship of specific rotation and concentration, and of molecular-solution-volume and concentration at 20°.*



condition. In octyl alcohol, the value of the molecular-solution-volume of ethyl tartrate at infinite dilution is apparently 174·3 c.c., or 3·4 c.c. greater than its molecular-volume, whilst the rotation, also at infinite dilution, is +5·24°, or 2·52° less than that of the free ester.

We thus obtain the figures on p. 484 for volume and rotation in the solvents so far examined.

Considering, now, the last five of these solvents, it appears that the results of the present investigation confirm those of the previous one. So long as the diminution of rotation continues in passing from one solvent to another, so long also does the molecular-solution-volume

Solvent.	M.S.V. infinite dilution, 20°.	Δ.	$[\alpha]_D^{20°}$, infinite dilution.	Δ.	Change in $[\alpha]_D^{20°}$ due to solution.
Water	157·7 c.c.		+26·15°		+18·49°
Glycerol	163·3 ,,		10·57		2·91
Methyl alcohol	159·3 ,,	4·7 c.c.	11·50	2·37°	3·84
Ethyl ,,	164·0 ,,	3·5 ,,	9·13	1·73	1·47
n-Propyl ,,	167·5 ,,	2·8 ,,	7·40	0·87	−0·26
*iso*Butyl ,,	170·3 ,,	4·0 ,,	6·53	1·29	−1·23
*sec.*Octyl ,,	174·3 ,,		5·24		−2·52

increase and the decrements of rotation correspond fairly closely with the increments of volume. The alteration of volume in passing from *iso*butyl alcohol to octyl alcohol is greater than in passing from *n*-propyl alcohol to *iso*butyl alcohol, and so is the rotational change, but had the intermediate members of the series been examined there is little doubt that the increments of volume and decrements of rotation would show a similar correspondence for each member as is the case for the first four.

The changes in volume and rotation appear to become simultaneously smaller, and probably both tend to some limiting values, which are, however, not the constants for free ethyl tartrate.

From the results so far obtained, it seems tolerably clear that water and glycerol, although they do fit into the above table, behave in a different manner from the monohydric alcohols. The rotation of ethyl tartrate in water is very much higher than would be expected from a comparison of the molecular-solution-volumes, and glycerol also shows differences, not quite so pronounced perhaps, which are most apparent in the form of the concentration-rotation curve. From this it may be surmised that, in addition to the volume change, there is a specific action of the solvent as well, so that volume relationships such as those described here only hold strictly for one series of solvents. It has been pointed out above, for instance, that although the molecular volume of ethyl tartrate is practically the same as its molecular-solution-volume in *iso*butyl alcohol, the specific rotations of the free ester and its solution are not identical. Now in part I. of this investigation (this vol., p. 198) it was pointed out that, in considering the rotation of an active substance in the homogeneous condition, the molecular rotation should be regarded as the rotation of the molecule subjected to the internal forces of that liquid, that is, the active compound should be looked upon as a solution in itself; if free ethyl tartrate be regarded thus and its rotation compared with

that of a solution in *iso*butyl alcohol, the difference in composition of the solvents is probably sufficient to explain the difference in rotation in the two cases, in spite of the fact that the volume is the same or very nearly the same in both. It is possible that a really strict coincidence would only be shown in solvents whose chemical composition is closely related to that of the active substance, but the decision of this question must be left to future investigation.

Although, as has just been explained, there appears to be a distinct relationship between molecular-solution-volume and rotation, inasmuch as they vary in a similar manner, no very marked correspondence is to be noticed between the shapes of the concentration-volume and concentration-rotation curves for the solvents whose behaviour is the subject of this paper. The volume curve for *iso*butyl alcohol, for instance, is almost a straight line, and so indeed is that for octyl alcohol, whereas the rotation curves dip considerably to reach a minimum at a certain concentration and then rise again. In the former communication, two similar instances were described, so that in four solvents at least* *n*-propyl alcohol, *iso*butyl alcohol, *sec.*octyl alcohol, and glycerol there exists for any particular temperature a concentration of ethyl tartrate for which the specific rotation is a minimum. Now if rotation depends proximately on volume, and, as appears to be the case for ethyl tartrate, diminishes with increase of volume, then it follows that when the specific rotation of ethyl tartrate in any solvent reaches a minimum, the molecular-solution-volume should have attained to a maximum value at the same concentration. The molecular-solution-volume curves in Fig. 3 show no such maximum value, but it does not necessarily follow that none exists, for the curves drawn represent, not only the change in volume of the ethyl tartrate, but also that of the solvent, both the changes, which may be opposite in sign, being attributed to the ethyl tartrate. Obviously, therefore, the occurrence of a maximum volume of the ethyl tartrate may be entirely masked by contraction in the solvent.

In the former paper (pp. 191—193), the behaviour of glycerol solutions of ethyl tartrate in this respect has been described. It was shown that in dilute solutions, as the concentration increases, the molecular-solution-volume also increases rapidly. When the proportion of ethyl tartrate in the mixture has risen to about 20 per cent., however, this rapid increase ceases (see this volume, Fig. 8, p. 180), the variation of volume with increase of concentration then becoming much more gradual. From a comparison of the corresponding curves for volume and rotation† it was suggested that in reality the ethyl

* There is possibly, also, a concentration of minimum rotation in ethyl alcohol, but it is not so well marked.

† This solvent shows a particularly well marked concentration of minimum rotation.

tartrate may continue to expand with increasing concentration—the glycerol contracting meanwhile—until a maximum volume of about 173 c.c. is reached, when $p = 65$, the specific rotation being then $+5{\cdot}2°$.

The results of the present investigation appear to support this suggestion, for they show that, not only is the volume of ethyl tartrate in octyl alcohol greater than the normal, but that its value at infinite dilution is 174·3 c.c., the rotation corresponding to this volume being $+5{\cdot}24°$, which is almost exactly the same as in glycerol at the concentration of minimum rotation. Thus for the same value of the rotation in two different solvents and at different concentrations the actual volume in one case (octyl alcohol at infinite dilution) corresponds closely with that predicted for the other (glycerol at $p = 65$) from the general appearance of its molecular-solution-volume curve.

In the other three instances, however, the molecular-solution-volume curves do not show such a rapid variation as is met with in glycerol, but then neither is the diminution of rotation with increase of concentration so striking, and it is quite possible that in these solvents also the volume of the ethyl tartrate reaches a maximum, when the rotation has fallen to a minimum, value. If this be the case, then since in *n*-propyl alcohol at 20° ethyl tartrate has a minimum rotation ($+6{\cdot}4°$) when $p = 57$, in *iso*butyl alcohol ($+5{\cdot}06°$) when $p = 45$, and in octyl alcohol ($+4{\cdot}28°$) when $p = 39$, the solution-volumes of the ester should have maximum values at the concentrations mentioned, but no proof that this is the case can at present be adduced. In the meantime, but little more can be done with regard to this interesting question than to give the data as stated. In the monohydric alcohols, the minimum rotation occurs at a less concentration the higher the molecular weight of the solvent. As a possible explanation, the above suggestion may be offered, as it seems to have more in its favour than any other which can at present be brought forward.

Of other views there are two which may be mentioned, and according to them change of rotation with variation of concentration depends (1) on simultaneous variation of association of the molecules of the active substance, or (2) on the formation of different chemical combinations of active substance and solvent. To both of these ideas there are considerable objections which need not be discussed here. Their *a priori* improbability (as applied to the cases under consideration, of course) is great, but what is perhaps more important, neither of them seems, at present, at least, to be verifiable. Any methods we now possess for the determination of molecular weight in solution can only be used when the dilution is great, and are incapable of being applied to trace the phenomena met with in these experiments, whilst there appears to be even less hope of demonstrating the actual existence of the compounds presupposed by the second theory which, if they are

formed, must be of a different order from anything we are acquainted with at present. To this same objection, the suggested correlation of volume and rotation may also be open, but it seems to allow room for greater hope of satisfactory demonstration, and experiments are being undertaken which may throw light upon this particular subject.

It would appear, then, that the results of this investigation tend to confirm the generalisation deduced from the former research. We seem to be justified in concluding that, at any rate in the seven solvents so far examined, a relationship does exist between molecular-solution-volume and specific rotation, but it also appears probable that this relationship only holds strictly throughout a particular series of solvents. In the present series, no influence is apparent which can be definitely attributed to the slightly different constitutions of the alcohols used.

In the previous paper, the variation of molecular-solution-volume was shown to agree with the variation of heat of disgregation of the solvent, but the want of sufficient data makes a comparison impossible in the present case, and a similar remark applies to the dielectric constants. Molecular weight determinations have not been carried out in the present instance, since these being necessarily made by the boiling point method, would only apply for temperatures considerably above those for which the rotation has been examined, and would therefore have comparatively little value.

Ethyl Tartrate in iso*Butyl Alcohol.*

The *iso*butyl alcohol used was obtained from Kahlbaum. It was distilled over sodium and then redistilled. Examined in a 400 mm. tube in the polarimeter, it was found to be inactive.

Determination of its density, relative to that of water at 4°, at various temperatures, gave these results:

Temperature	16·9°	41°	53·2°	69·6°	83·7°
Density.....	0·8053	0·7861	0·7759	0·7615	0·7482

By interpolation from these figures, the value 0·8029 at 20° is found.

Linnemann (*Annalen*, 1871, **160**, 238) gives d 18°/0° 0·8003.

$p = 5$.

Temperature.	α_D (400 mm.).	Density.	$[\alpha]^{t°}_D$.
25·6°	+1·132°	0·8116	+6·97°
13·5	0·828	0·8211	5·04
63·9	1·718	0·7799	11·02
53·9	1·570	0·7888	9·95
44·0	1·420	0·7971	8·91
27·3	1·168	0·8102	7·21
13·3	0·840	0·8212	5·11

Densities determined:

						After experiment.
Temperature	18·5°	31°	48°	63·8°	80·1°	19·9°
Density	0·8174	0·8076	0·7937	0·7798	0·7648	0·8165

$p = 9{\cdot}996$.

Temperature.	α_D (400 mm).	Density.	$[\alpha]^{t°}_D$.
20·5°	+1·899°	0·8307	+5·72°
16·9	1·755	0·8339	5·26
76·5	3·622	0·7823	11·58
69·2	3·509	0·7889	11·12
61·2	3·322	0·7956	10·44
50·2	3·037	0·8051	9·44
41·1	2·750	0·8130	8·46
27·4	2·245	0·8250	6·81
16·1	1·734	0·8345	5·20

Densities determined:

							After experiment.
Temperature	19·7°	30·8°	47°	65·6°	81·8°	83·4°	15·9°
Density.....	0·8311	0·8223	0·8087	0·7925	0·7774	0·7762	0·8343

$p = 25$.

Temperature.	α_D (400 mm.).	Density.	$[\alpha]^t_D$.
18·7°	+4·505°	0·8777	+5·13°
14·9	3·980	0·8809	4·52
63·2	8·686	0·8389	10·36
56·9	8·188	0·8441	9·70
48·9	7·556	0·8510	8·88
39·0	6·666	0·8600	7·75
26·0	5·328	0·8711	6·11
78·2	9·583	0·8249	11·62
73·2	9·291	0·8300	11·20
65·5	8·856	0·8365	10·59
18·1	4·402	0·8782	5·01
13·2	3·782	0·8826	4·28

Densities determined:

						After experiment.
Temperature	14·7°	26·6°	43·6°	59°	77·2°	14·8°
Density	0·8812	0·8704	0·8557	0·8423	0·8252	0·8806

$p = 50{\cdot}005$.

Temperature.	α_D (100 mm.).	Density.	$[\alpha]^t_D$.
12·7°	+1·968°	0·9713	+4·05°
43·3	3·813	0·9429	8·09
26·6	2·867	0·9584	5·98
18·0	2·322	0·9665	4·80
78·4	5·043	0·9102	11·08
70·2	4·738	0·9180	10·32
61·6	4·472	0·9260	9·66
52·2	4·122	0·9349	8·82
18	2·320	0·9665	4·80

Densities determined:

						After experiment.
Temperature.	16°	38·2°	52·5°	67·5°	77·6°	20°
Density	0·9683	0·9480	0·9345	0·9203	0·9104	0·9656

$p = 62{\cdot}84$.

Temperature.	α_D (100 mm.).	Density.	$[\alpha]^{t}_{D}$.
20°	+3·385°	1·0173	+5·29°
18	3·199	1·0193	4·99
82·3	6·920	0·9569	11·51
78·8	6·804	0·9601	11·28
72·2	6·530	0·9670	10·75
62	6·107	0·9770	9·95
52·5	5·630	0·9867	9·08
27·7	4·030	1·0102	6·35
39·8	4·907	0·9990	7·82
12	2·754	1·0248	4·28

Densities determined:

Temperature.....	17·4°	33·9°	47·3°	65°	82·8°
Density	1·0198	1·0044	0·9916	0·9741	0·9563

$p = 75{\cdot}03$.

Temperature.	α_D (100 mm.).	Density.	$[\alpha]^{t}_{D}$.
13·3°	+3·821°	1·0787	+4·72°
43·2	6·680	1·0493	8·49
29·1	5·418	1·0630	6·79
17·9	4·265	1·0741	5·29
88·0	8·756	1·0099	11·56
74·9	8·458	1·0181	11·07
62·5	7·815	1·0304	10·11
54·5	7·333	1·0383	9·41
15·7	4·061	1·0761	5·03

Densities determined:

						After experiment.
Temperature	18·4°	27·5°	44·3°	58·3°	78·8°	19·8°
Density	1·0738	1·0650	1·0486	1·0347	1·0142	1·0739

Ethyl Tartrate in sec.*Octyl Alcohol* (*Methylhexylcarbinol*).

The *sec.*octyl alcohol used was obtained from Kahlbaum, and was carefully distilled in a vacuum over well cleaned sodium. It boiled at 76° (bath 106°, pressure 11 mm.). Kahlbaum (quoted by Beilstein) gives 75·5° as the boiling point under 10·1 mm. pressure. Examined in the polarimeter, it was found to be distinctly active; in order that a correction might be made for this in the subsequent experiments, the

rotation of the alcohol was examined at several different temperatures, with the following results:

Temperature.	α_D (400 mm.).	Temperature.	α_D (400 mm.).
15·6°	−0·275°	67·3°	−0·265°
84	0·263	49·3	0·267

The density of the alcohol relative to water at 4°, at different temperatures, was as follows:

Temperature	18·1°	28·9°	36·9°	48·1°	60·8°	79·3°
Density	0·8212	0·8131	0·8070	0·7982	0·7880	0·7728

From these figures, the value 0·8198 at 20° is obtained by interpolation.

Brühl (*Annalen*, 1880, **203**, 28) gives d 20°/4° 0·8193.

$p = 5·001$.

Temperature.	α_D (400 mm.).	Corr.	Density.	$[\alpha]^{t}_{D}$.
18·9°	+0·535°	+0·264°	0·8335	+4·79°
41·3	0·968	0·261	0·8161	7·53
26	0·690	0·262	0·8280	5·75
12·8	0·438	0·265	0·8382	4·19

Densities determined:

Temperature.....	17·8°	32·6°	46·5°	61·7°	81°
Density	0·8342	0·8230	0·8122	0·7997	0·7835

$p = 10$.

Temperature.	α_D (400 mm.).	Corr.	Density.	$[\alpha]^{t}_{D}$.
18°	+1·288°	+0·273°	0·8478	+4·60°
76·4	3·141	0·263	0·8002	10·63
67·5	2·940	0·265	0·8076	9·92
54·9	2·588	0·267	0·8180	8·73
47	2·360	0·268	0·8242	7·97
25·6	1·590	0·272	0·8417	5·53
11·6	0·980	0·274	0·8530	3·68

Densities determined:

Temperature.....	18·4°	30·4°	47°	61·8°	78·8°
Density	0·8471	0·8379	0·8247	0·8123	0·7982

$p = 24{\cdot}997$.

Temperature.	α_D (249·6 mm.).	Corr.	Density.	$[\alpha]^{t°}_D$.
18°	+2·060°	+0·139°	0·8898	+3·96°
79·4	5·493	0·134	0·8383	10·76
72·9	5·243	0·135	0·8439	10·21
63·6	4·850	0·135	0·8519	9·38
56·1	4·513	0·136	0·8581	8·68
48	4·096	0·137	0·8650	7·84
41	3·708	0·137	0·8707	7·08
25·2	2·675	0·139	0·8837	5·10
12·1	1·682	0·140	0·8944	3·27

Densities determined:

Temperature ...	18·4°	32·2°	47·9°	64·4°	80·3°
Density.....	0·8895	0·8783	0·8652	0·8511	0·8374

$p = 50{\cdot}02$.

Temperature.	α_D (100 mm.).	Corr.	Density.	$[\alpha]^{t°}_D$.
11·5°	+1·492°	+0·041°	0·9790	+3·13°
44	3·525	0·041	0·9507	7·50
30·6	2·722	0·041	0·9627	5·74
17·3	1·902	0·041	0·9739	3·99
83	4·954	0·039	0·9148	10·91
77·5	4·867	0·040	0·9199	10·66
69·3	4·562	0·040	0·9277	9·92
58·2	4·135	0·040	0·9380	8·90
18·6	1·988	0·041	0·9728	4·17

Densities determined

Temperature..... ..	19·1°	34·4°	46·9°	66·6°	81°
Density	0·9728	0·9593	0·9481	0·9302	0·9168

$p = 75{\cdot}01$.

Temperature.	α_D (100 mm.).	Corr.	Density.	$[\alpha]^{t}_{D}$.
16·7°	+3·822°	+0·023°	1·0779	+4·76°
82·2	8·733	0·022	1·0158	11·50
76·3	8·447	0·022	1·0210	11·06
66·9	7·927	0·022	1·0300	10·29
53·3	7·075	0·022	1·0431	9·07
26·6	4·892	0·023	1·0687	6·14
11·9	3·289	0·023	1·0823	4·08
40·4	6·147	0·023	1·0556	7·79

Densities determined:

Temperature	17°	29·1°	50·1°	65·7°	81·6°
Density	1·0777	1·0663	1·0462	1·0312	1·0161

The data so far obtained for the monohydric alcohols should be sufficient to characterise their general behaviour; the author hopes soon to be in a position to communicate the results of experiments, at present being carried out, which shall do the same for other series of solvents.

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LIV.—*Metal-Ammonia Compounds in Aqueous Solution. Part II. The Absorptive Powers of Dilute Solutions of Salts of the Alkali Metals.*

By H. M. DAWSON and J. MCCRAE.

IN a previous communication (Trans., 1900, **77**, 1239), we have shown how the presence of certain salts affects the distribution of ammonia between water and chloroform. From the results obtained we were able to draw conclusions as to the composition of the complex ammonia derivatives existing in the aqueous ammoniacal solutions. In the course of this work the effect of the addition of sodium sulphate to ammoniacal copper sulphate solutions was investigated, with the view of determining the influence of an increase in the concentration of one of the electrolytic dissociation products of cupri-ammonia sulphate. Experiments had to be made to determine the influence of sodium sulphate alone on the distribution of ammonia between water and

chloroform, and it was found that this, although small, was appreciable.

From a study of the effect of dissolved electrolytes on the solubility of nitrous oxide, Gordon (*Zeit. physikal. Chem.*, 1895, **18**, 1) obtained results which, as Jahn (*ibid.*, p. 8) has shown, indicate that the influence of the dissolved salt is proportional to its concentration raised to the power 2/3, that is, to the number of molecules contained in unit area. If a is the absorption coefficient in pure water, a' that in the salt solution, and m the concentration of the salt expressed in molecules per litre, then

$$\frac{a-a'}{m^{\frac{2}{3}}} = \text{a constant.}$$

Gordon has also shown that Steiner's (*Ann. Phys. Chem.*, 1894, [iii], **52**, 275) results obtained for the solubility of hydrogen in solutions of electrolytes are in agreement with this relationship,

With the object of determining whether the solubility of ammonia in water is influenced in the same manner as is the solubility of nitrous oxide and of hydrogen by the addition of electrolytes, we have carried out a series of experiments with solutions of various alkali salts.

The influence of the dissolved electrolyte will, in the case of neutral inactive substances, be of a purely physical character, but if, as in the case of ammonia, the substance has not this neutral inactive nature, the simple physical action will be complicated by chemical action between added substance and electrolyte. The chemical action may be of two kinds: (1) partial displacement of the acidic (or basic) radicle of the salt by the base (or acid) added, and (2) formation of molecular compounds. In the special case of ammonia, the first chemical action is preceded by the action of the distributing substance on the solvent, but in consequence of the weak basic character of ammonia it can be shown that the former action is negligibly small.

In the case of solutions of salts of the alkali metals, it may be assumed as a working basis that no appreciable formation of additive compounds with ammonia takes place, in which case the only influence of the dissolved salt will be that resulting from what may be called the physical action. The relatively small tendency of most of the salts of the alkali metals to form ammonia additive products in the solid state justifies to a certain extent this assumption, but it is well to bear in mind that as yet no evidence of the non-formation of such compounds in aqueous solution has been brought forward.

Raoult (*Ann. Chim. Phys.*, 1874, [v], **1**, 263) has investigated the influence of dissolved salts on the solubility of ammonia in water. His experiments were carried out with very concentrated solutions, which were saturated with ammonia under atmospheric pressure. With

respect to ammonia, the solutions varied from 30 to 50 normal, and with respect to salt, from 2·5 to 10 normal. His results may be briefly stated as follows. Caustic potash and caustic soda decrease the solubility in a marked degree. Ammonium chloride exerts a similar influence but to a very much smaller extent, whilst ammonium and sodium nitrates have scarcely any effect. The presence of calcium nitrate very appreciably increases the solubility. In all cases the influence is proportional to the amount of salt in the solution. If the quantity of ammonia absorbed by 100 c.c. of water be denoted by C_w, that absorbed by 100 c.c. of salt solution containing g grams of salt by C_s, it is obvious that the results can be expressed by the equation

$$\frac{C_w - C_s}{g} = k$$

where k is a constant the value of which depends on the nature of the dissolved salt.

It is not probable that the values which might be deduced from Raoult's results could be used to express the influence of the dissolved salts on the absorptive power of water for ammonia, since on account of the high concentration the character of the solvent is so completely changed.

Our experiments have been carried out with much more dilute solutions, normal salt solutions being the most concentrated employed

With the object of determining the specific action exerted by various salts of the alkali metals, and the influence of the concentration of the salt solution on the distribution of ammonia between water and chloroform, a series of experiments was carried out in which the ammonia concentration in the aqueous phase was (nearly) constant, namely, about 0·5 normal, and a series in which the ammonia concentration varied.

Method.—Fifty c.c. of a solution containing known quantities of salt and ammonia were shaken with 100 c.c. of chloroform which had been treated with ammonia, then with dilute sulphuric acid, and finally distilled immediately before being used. After shaking in a thermostat at 20° until equilibrium was attained, the two layers were separated and titrated as described previously (former paper, *loc. cit.*) with 1/10th or 1/20th normal acid.

In our previous communication we have assumed that the coefficient of distribution of ammonia between chloroform and pure water is independent of the ammonia concentration. The results of Hantzsch and Sebaldt (*Zeit. physikal. Chem.*, 1899, 30, 258) seem to prove this, and the figures obtained by us also pointed to this conclusion.

During the course of the present investigation we were led to conduct experiments at higher ammonia concentrations than formerly.

Considerable experience in the carrying out of the determinations has enabled us to attain a much greater degree of accuracy than can be attached to the numbers referred to above, which were obtained at the commencement of our inquiry into this subject.

As a result of our new determinations, we can assert that the ratio of distribution of ammonia between water and chloroform is not quite independent of the ammonia concentration.*

The results obtained are given in the following table which contains, in addition to the ratio of the total ammonia concentrations (k), the ratio of the concentrations of the undissociated ammonia $\left(r = \frac{c_1(1-x)}{c_2}\right)$. The values of the degree of electrolytic dissociation (x) have been interpolated from the numbers in Hantzsch and Sebaldt's paper.

TABLE I.

Concentration of NH_3 in water. Grams per litre. c_1.	Concentration of NH_3 in $CHCl_3$. Gram per litre. c_2.	Distribution coefficient. $\frac{c_1}{c_2}$. k.	Degree of dissociation at concentration c_1. x.	$r = \frac{c_1(1-x)}{c_2}$. r.
5·160	0·1958	26·36	0·0077	26·15
6·393	0·2439	26·21	74	26·02
7·809	0·2979	26·21	71	26·03
7·861	0·2991	26·28	70	26·10
9·574	0·3677	26·04	68	25·86
12·081	0·4663	25·91	62	25·75
12·790	0·4962	25·78	60	25·62
14·410	0·5610	25·70	56	25·54
17·168	0·6780	25·32	50	25·19

From the experimental data and the appended curve (p. 497) it is clearly seen that at 20° the distribution coefficient diminishes somewhat as the ammonia concentration increases. The distribution coefficient would appear to be very nearly a linear function of the concentration, provided the latter (in the aqueous phase) is greater than 0·5 normal. As the concentration diminishes, the experimental difficulties of determining accurately the value of the distribution ratio increase proportionally. The figures obtained, however, indicate that for ammonia concentrations less than 0·5 normal the distribution coefficient is practically constant.

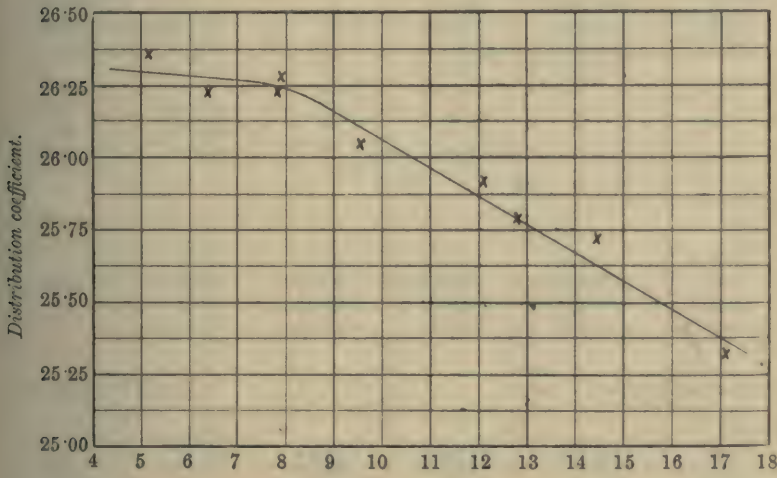
This is in harmony with the results of Jakowkin (*J. Russ. Phys.*

* It may here be pointed out that the variation of distribution coefficient with ammonia concentration does not appreciably influence the conclusions previously drawn concerning the amount of ammonia combined per molecule of salt.

Chem. Soc., 1900, **32**, 349; *Journ. Soc. Chem. Ind.*, 1900, **19**, 900), who finds that the partial pressure of ammonia solutions at 0° is proportional to the concentration so long as this does not rise above 0·5 normal, that is to say, at low pressures (where the amount of ammonia absorbed does not correspond to solutions more concentrated than 0·5 normal), ammonia obeys Henry's law.

The observed variation of the distribution coefficient (k) within the ammonia concentration limits employed is about 4 per cent. The variation of r is scarcely smaller than that of k and therefore electrolytic dissociation will not account for the diminution of distribution coefficient with increasing ammonia concentration.

Curve showing the dependence of distribution coefficient on ammonia concentration.



Concentration of ammonia in grams per litre in the aqueous solution.

Arrhenius (*Zeit. physikal. Chem.*, 1899, **31**, 197) has shown that the degree of dissociation of weak electrolytes is slightly increased in presence of strong electrolytes. On account of the difficulty of estimating the degree of dissociation of ammonia in salt solutions, the value of r in these cases cannot be accurately ascertained. In the investigation of the influence of dissolved salts on the absorptive power of water for ammonia, we compare (as indicated below), therefore, the values of k given by the respective solutions. Since, moreover, the difference between k and r is very small, the results which are obtained by a comparison of the values of k cannot differ sensibly from those which would be obtained by comparing the values of r.

The experimental results obtained with salt solutions are contained

in the following tables. As a rule, determinations were made with four different concentrations of each salt.

In the first series (Table II.) the ammonia concentration was constant (being about 0·45 normal), and the distribution coefficient would in all cases be 26·25. We have adopted this value for the calculation of the expression $\frac{k-k'}{n}$ (contained in the fifth column), where $k = 26{\cdot}25$, k' is the observed distribution coefficient with the salt solution of normality n (gram equivalent per litre).

TABLE II.

Strength of aqueous solution. n.	Concentration of NH_3 in the aqueous part, grams per litre. c_1.	Concentration of NH_3 in the $CHCl_3$, gram per litre. c_2.	Coefficient, $\frac{c_1}{c_2}$. k'.	$\frac{k-k'}{n}$.	Mean value of $\frac{k-k'}{n}$. δ.
Potassium iodide:					
0·4 *N*	7·779	0·3006	25·88	+0·92	
0·6	7·808	0·3044	25·65	1·00	1·02
0·8	7·799	0·3067	25·43	1·02	
1·0	7·791	0·3100	25·13	1·12	
Potassium bromide:					
0·6	7·800	0·3119	25·01	+2·07	
0·8	7·764	0·3161	24·56	2·11	2·13
1·0	7·780	0·3235	24·05	2·20	
Potassium nitrate:					
0·4	7·780	0·3101	25·09	+2·90	
0·6	7·805	0·3175	24·59	2·77	2·84
0·8	7·734	0·3240	24·03	2·78	
1·0	7·780	0·3335	23·33	2·92	
Potassium chloride:					
0·2	7·827	0·3055	25·62	+3·15	
0·4	7·836	0·3139	24·97	3·20	
0·6	7·800	0·3197	24·40	3·10	3·18
0·8	7·711	0·3252	23·71	3·18	
1·0	7·561	0·3291	22·98	3·27	

TABLE II. (*continued*).

Strength of aqueous solution. n.	Concentration of NH_3 in the aqueous part, grams per litre. c_1.	Concentration of NH_3 in the $CHCl_3$, gram per litre. c_2.	Coefficient, $\frac{c_1}{c_2}$. k'.	$\frac{k-k'}{n}$.	Mean value of $\frac{k-k'}{n}$. δ.
Potassium chlorate:					
0·25	7·734	0·3041	25·43	+3·28	3·28
Potassium oxalate:					
0·4	*7·724	0·3215	24·03	+5·55	5·72
0·6	*7·737	0·3412	22·68	5·95	
0·8	*7·660	0·3528	21·70	5·69	
1·0	*7·683	0·3741	20·54	5·71	
Potassium sulphate:					
0·2	7·742	0·3096	25·01	+6·20	6·17
0·4	7·776	0·3264	23·82	6·09	
0·4	7·773	0·3272	23·75	6·22	
Potassium carbonate:					
0·4	*7·850	0·3373	23·28	+7·42	7·15
0·6	*7·812	0·3560	21·94	7·18	
0·8	*7·772	0·3765	20·64	7·01	
1·0	*7·592	0·3938	19·28	6·97	
Sodium iodide:					
0·4	7·784	0·2951	26·37	−0·30	−0·32
0·6	7·764	0·2939	26·42	−0·29	
0·8	7·800	0·2944	26·50	−0·31	
1·0	7·805	0·2935	26·60	−0·35	
Sodium bromide:					
0·4	7·749	0·2999	25·84	+1·02	1·04
0·6	7·742	0·3018	25·64	1·01	
0·8	7·746	0·3048	25·40	1·06	
1·0	7·738	0·3070	25·21	1·04	

TABLE II. (*continued*).

Strength of aqueous solution. n.	Concentration of NH_3 in the aqueous part, grams per litre. c_1.	Concentration of NH_3 in the $CHCl_3$, gram per litre. c_2.	Coefficient, $\frac{c_1}{c_2}$. k'.	$\frac{k-k'}{n}$.	Mean value of $\frac{k-k'}{n}$. δ.
Sodium nitrate:					
0·4	7·734	0·3012	25·68	+1·42	
0·6	7·734	0·3061	25·27	1·63	
0·8	7·734	0·3111	24·86	1·74	1·65
1·0	7·734	0·3147	24·58	1·67	
1·0	7·698	0·3136	24·55	1·70	
Sodium chloride:					
0·4	7·820	0·3072	25·46	+1·98	
0·6	7·824	0·3124	25·05	2·00	
1·0	7·809	0·3232	24·16	2·09	2·04
1·0	7·709	0·3192	24·15	2·10	
Sodium chlorate:					
0·4	7·549	0·2975	25·38	+2·18	
0·6	7·657	0·3081	24·85	2·33	
0·8	7·716	0·3147	24·52	2·17	2·24
1·0	7·714	0 3214	24·00	2·25	
Sodium sulphate:					
0·4 (former paper, p. 1248)	7·233	0·2979	24·28	+4·92	
0·6	7·788	0·3360	23·20	5·09	
0·8	7·789	0·3529	22·08	5·21	5·12
1·0	7·724	0·3658	21·11	5·14	
Sodium carbonate:					
0·6	*7·728	0·3418	22·61	+6·07	
0·8	*7·679	0·3600	21·32	6·16	
0·8	*7·704	0·3616	21·30	6·19	6·08
1·0	*7·666	0·3770	20·33	5·92	

TABLE II. (*continued*).

Strength of aqueous solution. n.	Concentration of NH_3 in the aqueous part, grams per litre. c_1.	Concentration of NH_3 in the $CHCl_3$, gram per litre. c_2.	Coefficient, $\frac{c_1}{c_2}$. k'.	$\frac{k-k'}{n}$.	Mean value of $\frac{k-k'}{n}$. δ.
Lithium chloride :					
0·6	7·789	0·2872	27·12	−1·45	
0·8	7·766	0·2832	27·42	−1·46	1·46
1·0	7·767	0·2801	27·73	−1·48	
Lithium sulphate :					
0·4	7·812	0·3079	25·39	+2·15	
0·6	7·752	0·3110	24·92	2·21	
0·8	7·774	0·3187	24·39	2·32	2·16
1·0	7·759	0·3197	24·28	1·97	
Ammonium bromide :					
0·4	7·814	0·2966	26·36	−0·28	
0·6	7·756	0·2934	26·43	−0·30	
0·8	7·808	0·2942	26·54	−0·36	−0·35
1·0	7·812	0·2923	26·73	−0·48	
Ammonium nitrate :					
0·4	7·762	0·2985	26·00	+0·62	
0·6	7·665	0·2963	25·86	0·65	
0·8	7·738	0·3006	25·74	0·64	0·60
1·0	7·698	0·2988	25·76	0·49	
Ammonium chloride :					
0·8	7·816	0·3058	25·56	+0·86	
1·0	7·823	0·3081	25·39	0·86	0·88
1·0	7·812	0·3084	25·33	0·92	

TABLE II. (*continued*).

Strength of aqueous solution. n.	Concentration of NH_3 in the aqueous part, grams per litre. c_1.	Concentration of NH_3 in the $CHCl_3$, gram per litre. c_2.	Coefficient, $\frac{c_1}{c_2}$. k'.	$\frac{k-k'}{n}$.	Mean value of $\frac{k-k'}{n}$. δ.
Ammonium sulphate:					
0·4	7·902	0·3227	24·48	+4·42	
0·4	7·773	0·3180	24·44	4·52	
0·6	7·806	0·3292	23·71	4·23	
0·8	7·839	0·3426	22·89	4·20	4·2 ?
0·8	7·760	0·3380	22·96	4·12	
1·0	7·769	0·3491	22·25	4·00	
1·0	7·764	0·3481	22·30	3·95	
Potassium hydroxide:					
0·213	*7·878	0·3227	24·41	+8·64	about
0·284	*7·864	0·3295	23·86	8·41	8
Sodium hydroxide:					
0·36	*7·862	0·3315	23·71	+7·06	
0·54	*7·832	0·3463	22·61	6·74	6·6 ?
0·72	*7·802	0·3613	21·59	6·33	
0·90	*7·774	0·3753	20·71	6·16	

* In the case of the oxalates, carbonates, and hydroxides, the ammonia in the aqueous solution was not determined directly, but was calculated from the amount known to be originally present less the quantity which had gone into solution in the chloroform.

In the following table are given the results obtained with salt solutions containing smaller and larger quantities of ammonia than those used in the experiments recorded in Table II. The fifth column contains the values of k (the distribution coefficient for pure water at concentration c_1) obtained from the curve, and this was used in the calculation of the value of the expression $\frac{k-k'}{n}$ of the sixth column.*

* In the light of the more recent work incorporated in this paper, we find that when allowance is made for the variation of the distribution of ammonia between pure water and chloroform with the concentration, the irregularity noted in the

TABLE III.

n.	c_1.	c_2.	k'.	k.	$\frac{k-k_0}{n}$.	δ.
Potassium nitrate:						
0·6	11·136	0·4604	24·17	25·95	+2·93	
0·8	11·070	0·4688	23·61	25·95	2·92	
1·0	11·070	0·4794	23·09	25·95	2·86	2·81
0·6	13·910	0·5769	24·11	25·70	2·65	
0·8	13·880	0·5914	23·46	25·70	2·80	
1·0	13·860	0·6030	22·97	25·70	2·73	
Potassium chloride:						
1·0	6·194	0·2696	22·97	26·29	+3·32	
0·6	11·071	0·4628	23·92	25·95	3·38	
0·8	11·090	0·4765	23·27	25·95	3·35	
1·0	11·053	0·4899	22·56	25·95	3·39	3·38
0·6	13·853	0·5848	23·69	25·70	3·35	
0·8	13·835	0·6023	22·97	25·70	3·41	
1·0	13·831	0·6206	22·29	25·70	3·41	
Sodium sulphate:						
0·6	4·596	0·1988	23·12	26·33	+5·35	
0·8	4·577	0·2062	22·19	26·33	5·18	5·22
1·0	4·562	0·2152	21·20	26·33	5·13	
Lithium chloride:						
0·6	10·890	0·4081	26·69	25·97	−1·20	−1·20
Ammonium sulphate:						
0·8	5·581	0·2418	23·08	26·31	+4·04	
0·8	13·870	0·6138	22·59	25·70	3·89	3·97
0·8	13·870	0·6173	22·47	25·70	4·04	

An inspection of the tables shows that, with the exception of lithium chloride, ammonium bromide, and sodium iodide, all the salts investigated produce a lowering of the distribution coefficient; in other

Proceedings (1901, **17**, 6, lines 13 to 17) disappears. We desire, therefore, to withdraw the former statement referring to the behaviour of the more concentrated ammonia solutions.

words, the solvent power of aqueous solutions of the alkali salts is in general less than that of pure water.

Excepting the ammonium salts and the hydroxides, the dependence of the action exerted by a given salt on its concentration is clearly seen from the values of $\frac{k-k'}{n}$, contained in the fifth or sixth column. For solutions in which the concentration of the dissolved salt varies from 0·4 normal to normal, the value of this expression remains practically constant. In general, the variations from the mean value are quite irregular and cannot be represented as a function of the concentration; the change of the distribution coefficient is therefore proportional to the concentration of the salt.

The ammonium salts and hydroxides investigated would appear to behave differently. In the case of the sulphate, nitrate, and bromide of ammonium and the hydroxides of potassium and sodium, the value of $\frac{k-k'}{n}$ decreases with increasing salt concentration. That this variation cannot be attributed to errors of experiment is conclusively proved by the good agreement between the numbers obtained in two separate experiments (ammonium sulphate) carried out with the same salt concentration.

With this limitation, it appears legitimate, therefore, in the case of the salts investigated, to take the mean value of $\frac{k-k'}{n}$, that is δ, as a measure of the action exerted by the salt on the absorptive power of water for ammonia. This mean value we propose to designate the 'equivalent alteration of the distribution coefficient' for the salt under consideration; it is evident that this factor is proportional to the alteration of the partial pressure of ammonia produced by the dissolved salt in normal solution.

In view of the above-mentioned behaviour of the ammonium salts and the hydroxides, the mean value of $\frac{k-k'}{n}$ has not the same simple significance and cannot be regarded as an accurate measure of the specific action exerted by the salt. For the purpose of comparing the whole of the salts investigated, we have, however, considered it permissible to take a mean value in these cases also, more especially as the law regulating the variation of $\frac{k-k'}{n}$ with the concentration for the ammonium salts is not apparent from the experiments we have made.

The value which we take as a measure of the equivalent alteration of the distribution coefficient is the simple mean of the separate values, although the errors associated with the determination of $\frac{k-k'}{n}$

decrease considerably with increasing concentration. The values of δ so obtained are given in the following table, in which the cationic components of the salts are arranged horizontally and the anionic components vertically. The order of these is such that the value of δ decreases from left to right and increases from top to bottom.

TABLE IV.

	Potassium.		Sodium.		Ammonium.		Lithium.	
Iodides	1·0	(1·3)	−0·3					
Bromides	2·1	(1·1)	1·0	(1·3)	−0·3			
Nitrates	2·8	(1·1)	1·7	(1·1)	0·6			
Chlorides	3·2	(1·2)	2·0	(1·1)	0·9	(2·6)	−1·5	
Chlorates	3·3	(1·1)	2·2					
Oxalate	5·7							
Sulphates	6·2	(1·1)	5·1	(0·9)	4·2?	(2·0)	2·2	
Carbonates	7·2	(1·1)	6·1					
Hydroxides	8?		6·6?					

The numbers in brackets are the differences between the values of δ in the successive vertical columns. It is at once evident that the differences between the values of δ for a series of salts in which the same two basic radicles are united with different acid radicles are constant. The mean difference between the potassium and sodium salts investigated is 1·2, between the sodium and ammonium salts 1·1, and between the ammonium and lithium salts 2·3.

Exactly similar regularities are observable on comparing any two series of salts in which the same two acid radicles are combined with the various alkali metals. For example, the difference between the chloride and bromide of potassium is 1·1, of sodium it is 1·0, and of ammonium it is 1·2.

It may be noticed that the numbers obtained by Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 985 ; *Chem. Centr.*, 1900, i, 938) for the ammonia partial pressure of ammoniacal salt solutions show traces of these additive relationships. The partial pressures of normal ammonia solutions containing 1 gram equivalent of salt per litre were determined at 60° by the dynamical method. In the table (p. 506), the values of $P_1 - P$ are given, P_1 denoting the pressure of ammonia over pure water and P that over the salt solution.

Gaus (*Zeit. anorg. Chem.*, 1900, **25**, 236) has also investigated the ammonia pressure of salt solutions in a similar manner at 25°, the concentration of the solutions being 0·4 normal with respect to salt, and normal with respect to ammonia. The values of $P_1 - P$ (same as above) are tabulated below, and for comparison the values of δ obtained

TABLE V.

	Potassium.	Sodium.	Ammonium.	Lithium.
Iodide	2·4			
Bromide	5·6			
Nitrate	5·8			
Chlorides	7·7	4·4	2·0	−2·7
Oxalate	13·8			
Sulphates	11·1		7·1	
Carbonates	17·1	13·9		
Hydroxides	19·1	15·3		

by us are appended. With a single exception (potassium chloride), the order of the salts is the same in both series, and the same degree of parallelism is observable if Konowaloff's series is compared with that contained in Table IV.

TABLE VI.

Salt:	NaOH.	$(NH_4)_2SO_4$.	$(NH_4)_2C_2O_4$.	KCl.	NaCl.	NH_4Cl.	NH_4NO_3.	NH_4I.
$P_1 - P$:	+1·51	+0·97	+0·82	+1·00	+0·79	+0·09	−0·02	−0·25
δ:	+6·66	+4·2	+3·5*	+3·2	+2·0	+0·9	+0·6	−1·4*

* Estimated.

The existence of the above regularities, which are of exactly the same nature as those found for many other properties of dilute solutions, indicates that the influence of dissolved alkali salts on the solvent power of water for ammonia is capable of being represented as the sum of two factors, one of which is dependent only on the cation of the salt, the other only on the anionic component. A knowledge of the value of these factors for the various ions enables us to predict with certainty the influence which would be exerted by the alkali salts not investigated.

Before the significance of the numbers contained in Table IV is further discussed, it is necessary to ascertain to what extent they may be affected by the displacement of the base contained in the salt by the ammonia added. If in a solution there are present equivalent quantities of two slightly dissociated bases and an acid, the ratio of distribution of the bases will be that of their degrees of dissociation at the concentration of the solution under consideration. Although this proportionality does not exist in the case when one of the bases is highly dissociated, yet it may be assumed to be so for our purpose.

In 0·5 normal solution, which represents the approximate concentration of the solutions used in our experiments both in regard to salt and to ammonia, the hydroxides of potassium, sodium and lithium are dissociated approximately to the extent of 80 per cent., whilst the dissociation of ammonium hydroxide is only about 0·7 per cent. From this consideration, it is apparent that the disturbing effect of this distributing action in our case is very small. In a discussion of Setschenoff's (*Zeit. physikal. Chem.*, 1889, **4**, 117) experiments on the solubility of carbon dioxide in salt solutions, Rothmund (*Zeit. physikal. Chem.*, 1900, **33**, 402) rightly points out that in this case also the disturbing effect of chemical action with salts of strong acids can be totally neglected.

In the case of solutions containing ammonium salts, the chemical action considered above completely disappears, but then one of the products of electrolytic dissociation of the dissolved salt is identical with the positive ion of the base formed by interaction of the distributing substance with the solvent. As in the previous case, however, the smallness of the percentage of ammonium ions in an aqueous solution of ammonia renders the effect produced by the presence of an ammonium salt negligibly small. To show still more clearly that the system investigated by us is of a simple character and is not materially affected by the complicating influences just mentioned, it is sufficient to note that an aqueous solution of ammonia contains probably for the most part molecules of the formula NH_3 of the same complexity as those in the gaseous state. A number of facts indicate that the proportion of ammonia molecules which enter into chemical combination with water molecules with production of ammonium hydroxide is very small, and it seems probable, moreover, that the degree of electrolytic dissociation referred to the ammonium hydroxide in solution, and not to the total quantity of ammonia, is of the same order of magnitude as that of the alkali hydroxides.

Table IV shows that sodium iodide increases the solvent power of water for ammonia, and from the observed regularities we can conclude that this is the case for ammonium iodide and bromide, and in a still greater degree for lithium iodide, bromide, nitrate, and chloride. The behaviour of these salts is analogous to that of the copper, zinc, cadmium, and nickel compounds investigated by us previously (*loc. cit.*), in which cases we have proved conclusively the formation of additive compounds with ammonia. The assumption of the formation of similar complexes in the above cases does not therefore appear to be an improbable one, and is supported by a number of facts. The lithium halides form a series of fairly stable solid additive compounds with ammonia, and ammonium nitrate absorbs ammonia readily at low temperatures, with production of a similar complex. The increase in

the solvent power for ammonia brought about by lithium salts is similar to that produced by magnesium, calcium, and strontium salts, and this behaviour is in agreement with many other chemical properties of the compounds of lithium. The observed behaviour of lithium compounds is therefore in complete accord with the position occupied by lithium in the periodic system, approximating in its chemical characteristics as a member of the first short period to the members of the second group.

These considerations lead us to conclude that the experimental data for the action of the various alkali salts probably do not give us an accurate measure of the physical action exerted by the salts. The values of δ represent the superposed influences of physical action and of the formation of chemical complexes, and the relative magnitude of this latter factor cannot be easily determined. It may with safety be assumed that it is greatest in the case of the lithium salts, and is probably very small for potassium salts.

According to the views of Abegg and Bodländer (*Zeit. anorg. Chem.*, 1899, 20, 453), it would appear that ammonia in its capacity of forming the neutral component of complex ions is only able to combine with positive ions, whilst negative ions are not capable of forming such an ammonia complex. If such be the case, then the differences between the values of δ for the various salts of any one metal must be regarded as expressing the differences in the purely physical action of the various anions. On the other hand, the differences between the values of δ for the series of salts of any one acid have not this simple significance by reason of the cationic complex formation.

From the table (IV) it is evident that the greatest effect is produced by the SO_4 and CO_3 ions, whilst the I, Br, and NO_3 ions are least effective.

A parallel behaviour has been found in several other investigations on the influence of dissolved salts on the solubility of other non-electrolytic substances. Rothmund (*loc. cit.*) has given a summary of these researches, in which the solubility of hydrogen, nitrous oxide, carbon dioxide, ethyl acetate, and phenyltbiocarbamide have been investigated, and has shown that the order in which the dissolved electrolytes arrange themselves according to the magnitude of their influence on the solubility is the same in the case of each of these substances. The sulphates and carbonates exert the greatest action, the chlorides and nitrates less, exactly as we find in the case of ammonia.

The fact that so many experimental investigations lead to the same result in regard to the activity of the anions of dissolved electrolytes in their influence on the solubility of non-electrolytes, is of fundamental significance for the theory of solution. The constancy of the

phenomena, in spite of the varying nature of the dissolved non-electrolyte, points to a change in the character of the solvent.

In the investigations mentioned, the cations of the dissolved salts appear to exert a considerably smaller influence than the anions on the solubility of the non-electrolytes; the results indicate, however, that ammonium and lithium are less active than potassium and sodium, which accords with the results of our experiments.

In an investigation carried out to elucidate the nature of aqueous ammonia and amine solutions, Hantzsch and Sebaldt (*Zeit. physikal. Chem.*, 1899, **30**, 258) determined the effect of the addition of ammonium chloride to the aqueous solution of ammonia on the amount of ammonia removed from the latter by chloroform. The molecular ratio NH_3 to NH_4Cl varied from 1 : 0 to 1 : 8. They state that, "in allen Fällen war fast genau die gleiche Menge Ammoniak in das Chloroform übergegangen, gerade so als ob das Chlorammonium gar nicht vorhanden gewesen wäre. Dies läuft allen bisher gemachten Versuchen zuwider nach welchen durch vermehrten Zusatz des Salzes die Dissociation der Base zurückgedrängt, mithin ein steigender Zuwachs derselben von dem zweiten Lösungsmittel aufgenommen werden müsste." The apparent absence of any influence is to be found in the very small proportion of ions in an aqueous ammonia solution, and, according to our results, in the small value of δ (0·9) for ammonium chloride, whereby the effect produced by the salt is completely overshadowed by the errors of experiment attending the determinations of these authors.

The addition of ammonium salts or the hydroxide of potassium or sodium does not produce an effect which is directly proportional to the amount of salt added. On the contrary, the value of $\frac{k-k'}{n}$ decreases with increasing salt concentration, as has been remarked on p. 504. These substances contain an ion common to ammonium hydroxide; as a result of the mass action of this common ion, the electrolytic dissociation of the ammonium hydroxide will be diminished, resulting in an increase in the concentration of the undissociated ammonia molecules, as is represented by the expression:

$$NH_4^{\cdot} + OH' \rightleftarrows NH_4OH \rightleftarrows NH_3 + H_2O,$$

passing from left to right. It is impossible, however, to account for the anomalous behaviour of the substances on this ground, because, even if the introduced ion forced the dissociation to recede completely, the concentration of ammonia molecules could not be altered to a greater extent than a fraction of a per cent., whilst a difference of 1 per cent. on the numbers obtained, no matter how applied, would

not yield a constant for the value of $\frac{k-k'}{n}$. It would appear, therefore, that the ionic theory is not capable of explaining this different behaviour of the ammonium salts and the alkali hydroxides.

In his paper on the absorption of nitrous oxide, Roth (*Zeit. physikal. Chem.*, 1897, **24**, 114) has on theoretical grounds made the deduction that the solubility of a non-electrolyte should be the same in dilute solutions of other substances as in pure water; in other words, Dalton's law should be valid. The experimental investigation of solutions of some non-electrolytes has shown that this requirement of theory is approximately satisfied. In the case of solutions of electrolytes, much greater deviations have been observed, the influence of the dissolved electrolyte with respect to concentration being expressed by the purely empirical formula, $\frac{a-a'}{m^{\frac{2}{3}}}$, given by Jahn (see p. 494), or, according to our experience, in the case of ammonia, by the expression $\frac{k-k'}{n}$.*

From our experiments with ammonia, it would appear possible (see Table IV) to have solutions of electrolytes the solvent power of which is not appreciably different from that of pure water. The effectiveness of dissolved electrolytes is dependent upon the special character of their ionic components.

We have finally investigated the action of two non-electrolytes—urea and cane sugar—on the ammonia distribution, and the results are contained in the following table ($k = 26{\cdot}25$) :

TABLE VII.

n.†	c_1.	c_2.	k'.	$\frac{k-k'}{n}$.
Urea :				
0·6	7·857	0·3089	25·43	+1·37
1·0	7·866	0·3149	24·98	1·27
Cane sugar :				
0·4	7·799	0·3084	25·29	+2·40
0·5	7·829	0·3116	25·12	2·26

† Mol. per litre.

* It is hardly necessary to point out that Jahn's formula does not give a constant when applied to our results.

The effect of the dissolved non-electrolyte is therefore quite considerable, and greater than that produced by many of the alkali salts investigated. It apparently depends upon the specific character of the dissolved substance, and its variation with the concentration is the same as that found for the alkali salts.

In the case of non-electrolytes as well as of electrolytes, therefore, Dalton's law is not obeyed, and the changes which are apparently produced in the character of the solvent remain to be explained.

In our former paper, no account was taken of the physical action of the dissolved material, but the alteration of distribution coefficient caused by this is negligibly small in the case of copper, zinc, cadmium, and nickel salts compared with that due to the formation of complexes. The physical action in these cases is that of the complex compound existing in solution, and it is impossible to accurately estimate the value of this. Even if the physical action be as great as that of any of the salts of the alkali metals examined, the conclusions arrived at in our previous communication would not be altered, whilst the actual numbers expressing the ratio of the ammonia combined per molecule of salt would be increased by not more than 2—3 per cent.

THE YORKSHIRE COLLEGE,
LEEDS.

LV.—*Influence of a Heterocyclic Group on Rotatory Power; the Ethyl and Methyl Esters of Dipyromucyltartaric Acid.*

By PERCY F. FRANKLAND and FRANCIS W. ASTON, late Forster Research Scholar.

It has been shown by one of us that there is a great qualitative and quantitative difference in the rotatory effect of fatty acid groups (acetyl, chloracetyl, dichloracetyl, trichloracetyl, propionyl, phenacetyl, &c.) on the one hand, and of aromatic acid groups (benzoyl and toluyl) on the other, as exemplified by the rotatory power of the esters of the various diacyl tartaric and glyceric acids, and of the several acyl malic acids. The following table illustrates the difference in question :

Methyl glycerate [1]	$[\alpha]_D^{15^\circ}$	$-4{\cdot}80^\circ$	$[M]_D^{15^\circ}$ $-5{\cdot}76^\circ$
,, diacetylglycerate [2]		$-12{\cdot}04$	$-24{\cdot}56$
,, di-monochloracetylglycerate [3] .		$-12{\cdot}91$	$-36{\cdot}1$

[1] P. Frankland and Macgregor, Trans., 1893, **63**, 513.
[2] *Ibid.*, 1422.
[3] P. Frankland and Patterson, Trans., 1898, **73**, 197.

Methyl di-dichloracetylglycerate [1]	$[\alpha]_D^{15°}$ − 13·96°	$[M]_D^{15°}$ − 47·7°
„ di-trichloracetylglycerate [1]	− 14·20	− 58·3
„ dipropionylglycerate [2]	− 10·97	− 25·45
„ diphenacetylglycerate [2]	$[\alpha]_D^{14·5°}$ − 16·06	$[M]_D^{14·5°}$ − 57·17
„ dibenzoylglycerate [2]	$[\alpha]_D^{15°}$ + 26·89	$[M]_D^{15}$ + 88·20
„ di-*o*-toluylglycerate [3]	$[\alpha]_D^{20°}$ + 20·19	$[M]_D^{20°}$ + 71·9
„ di-*m*-toluylglycerate [3]	+ 26·40	+ 94·0
„ di-*p*-toluylglycerate [3]	+ 41·21	+ 146·7
	$[M]_D^{20°}$.	$[M]_D^{100°}$.
Diethyl tartrate	+ 15·86°	+ 27·6°
„ diacetyltartrate [4]	+ 9·9	+ 18·3
„ di-monochloracetyltartrate [5]	+ 25·5	+ 39·4
„ di-dichloracetyltartrate [5]	+ 65·8	+ 68·9
„ diphenacetyltartrate [4]	+ 79·2	+ 39·9
„ dibenzoyltartrate [6]	− 247·1	− 251·6
„ di-*o*-toluyltartrate [6]	− 266·5	− 241·9
„ di-*m*-toluyltartrate [6]	− 306·3	− 281·7
„ di-*p*-toluyltartrate [6]	− 484·4	− 397·7

The qualitative difference in rotatory effect between the fatty and aromatic acid radicles is similarly manifested in the following series of the derivatives of diethyl malate:

Diethyl malate [8]	$[\alpha]_D^{20°}$ − 10·44°	$[M]_D^{20°}$ − 19·84°
„ acetylmalate [7]	− 22·52	− 52·25
„ propionylmalate [7]	− 22·20	− 54·61
„ butyrylmalate [7]	− 22·22	− 57·77
„ *iso*butyrylacetate [7]	− 21·99	− 57·17
„ *iso*valerylmalate [7]	− 22·07	− 60·47
„ bromacetylmalate [7]	− 22·48	− 69·91
„ benzoylmalate [8]	$[\alpha]_D^{21°}$ − 3·87	$[M]_D^{21}$ − 11·38
„ *o*-toluylmalate [8]	− 6·25	− 19·25
„ *m*-toluylmalate [8]	− 4·67	− 14·38
„ *p*-toluylmalate [8]	$[\alpha]_D^{20°}$ − 0·22	$[M]_D^{20°}$ − 0·68

Similarly, in the derivatives of ethyl sarcolactate, we find the same relations exhibited (P. Frankland and Henderson, Proc., 1895, 11, 54):

[1] P. Frankland and Patterson, Trans., 1898, **73**, 197.
[2] P. Frankland and Macgregor, Trans., 1896, **69**, 117.
[3] P. Frankland and Henry Aston, Trans., 1899, **75**, 493.
[4] McCrae and Patterson, Trans., 1900, **77**, 1098, 1103.
[5] P. Frankland and Patterson, Trans., 1898, **73**, 189, 191.
[6] P. Frankland and Wharton, Trans., 1896, **69**, 1591.
Walden, *Zeit. physikal. Chem.*, 1895, **17**, 245—266.
[8] P. Frankland and Wharton, Trans., 1899, **75**, 337—347.

Ethyl sarcolactate	$[\alpha]_D^{15°}$ −8·66°	$[M]_D^{15°}$ −10·22°
,, acetyllactate.....	−41·47	−66·35
,, benzoyllactate	+22·22	+49·33

The lactic acid from which these compounds were prepared was afterwards found to be partially racemised, so that the absolute values given for the rotations are, of course, too small, but the ratios are probably, and the qualitative relations certainly, correct.

The monoacyl derivatives of diethyl tartrate form another series in which a comparison of the rotatory effect of the fatty and aromatic acid radicles has been rendered possible through the recent preparation of the monoacetyl and monophenacetyltartrates by McCrae and Patterson. Thus:

	$[M]_D^{20°}$.	$[M]_D^{100°}$.
Diethyl tartrate	+15·86°	+27·6°
,, monoacetyltartrate [1].....	+23 1	+33·5
,, mono-monochloracetyltartrate [2].	+32·3	+48·9
,, mono-trichloracetyltartrate [3] ...	+54·7	+61·7
,, monophenacetyltartrate [1].....	+98·5	+77·8
,, monobenzoyltartrate [4]	+61·4	+54·8
,, mono-*o*-toluyltartrate [4].....	+38·2	+35·3
,, mono-*m*-toluyltartrate [4]	+44·0	+40·8
,, mono-*p*-toluyltartrate [4].....	+63·5	+51·2

This series, in which the qualitative effect of all the acid radicles, both fatty and aromatic, appears similar, consisting as it does in raising the initial rotation of the diethyl tartrate, has been recently discussed by McCrae and Patterson (*loc. cit.*), who point out that the qualitative difference between the rotatory effect of the two classes of acid radicles only becomes apparent when the effect of introducing one and two acid radicles respectively is compared. Thus the introduction of a second fatty acid group (including phenacetyl) causes only a comparatively small diminution in the dextrorotation of the monoacyl compound, whilst the introduction of the second aromatic acid radicle (benzoyl and toluyl) gives rise to such an enormous diminution in the dextrorotation that the resulting diacyl compound is powerfully lævorotatory. Judged by the standard of the influence of temperature on the rotations, it is seen that all the fatty acyl compounds of this series, as of the other, have their rotation increased by rise of tempera-

[1] McCrae and Patterson, Trans., 1900, **77**, 1096—1110.

[2] P. Frankland and Turnbull, Trans., 1898, **73**, 204. It should be noted that the preparation was not quite pure, and that the real rotation is doubtless greater.

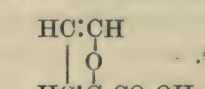
[3] P. Frankland and Patterson, Trans., 1898, **73**, 186.

[4] P. Frankland and McCrae, Trans., 1898, **73**, 307—329.

ture, whilst the aromatic acyl (including phenacetyl) compounds have their rotation diminished by rise of temperature. In the series of the diacyl ethyl tartrates, there is in this respect a curious, and so far as we are aware, unique anomaly presented by diethyl benzoyltartrate, the rotation of which attains a maximum for a temperature of about 60° (P. Frankland and Wharton, Trans., 1896, 69, 1587).

The marked qualitative contrast in rotatory effect between the isomeric phenacetyl and toluyl groups is doubtless to be referred to their structural difference, the carbonyl group being attached to the benzene ring directly in the case of the toluyl, and only indirectly in the case of the phenacetyl group. It becomes, therefore, of interest to know whether other cyclic groups besides the benzene ring have the power of conferring a rotatory effect qualitatively similar to that of the benzoyl and toluyl radicles.

With the view of determining this point, we have investigated the rotatory effect of the pyromucyl group, in which the carbonyl is directly attached to the heterocyclic furfuran ring:



Pyromucic acid.

In connection with this investigation, we have introduced advantageous modifications in the methods of preparing pyromucic acid and pyromucyl chloride.

By means of the latter we have prepared diethyl and dimethyl-dipyromucyltartrates, but have so far only determined the rotatory power of the former.

The rotatory power of diethyl dipyromucyltartrate was found to be almost exactly intermediate between those of diethyl dibenzoyltartrate and diethyl di-*m*-toluyltartrate, namely, $[M]_D^{99\cdot5^\circ} = -266\cdot5^\circ$. The rotatory effect of the heterocyclic furfuran ring is thus shown to be qualitatively similar to, and quantitatively of the same order as, that of the homocyclic benzene ring.

The qualitative similarity in rotatory effect of the pyromucyl, benzoyl, and toluyl groups is further exemplified by the fact that all the compounds referred to which contain these groups have their rotation diminished by rise of temperature, whilst those containing the fatty acid radicles* increase in rotatory power as the temperature rises; in

* In respect of the effect of temperature, the dichloracetyl and trichloracetyl groups approximate to the phenacetyl radicle; thus the rotation of ethyl di-dichloracetyltartrate is almost insensitive to temperature, whilst methyl di-dichloracetyltartrate has its rotation slightly diminished by rise of temperature; ethyl di-trichloracetylglycerate, again, has its rotation slightly diminished by rise of temperature.

this respect, however, it should be noticed that the phenacetyl group resembles the other aromatic and not the fatty groups. In fact the influence of temperature on rotatory power appears to differentiate between those compounds which contain and those which do not contain a cyclic group. This is at any rate true so far as the derivatives of glyceric and tartaric acids are concerned, and for these alone has this influence of temperature on rotation been fully investigated. In the case of malic acid, the aromatic acid derivatives increase in rotatory power with rise of temperature, but the influence of temperature on the fatty acid derivatives has not yet been determined.

We have in the course of this investigation devised a new method of continuous automatic esterification, by means of which we have prepared the methyl and ethyl tartrates which were required; this we think may be found of wide application in the preparation of esters.

Experimental.

Preparation of Pyromucic Acid.—The method first adopted was that described by Volhard (*Annalen*, 1891, **261**, 380), which consists in acting on furfural with alkaline permanganate. This, although yielding good results with small quantities, was found to be extremely laborious when a large amount of the acid was to be prepared in one operation. Thus the pyromucic acid is formed in an extremely dilute solution, and its separation from the potassium chloride with which it is mixed cannot be effected by crystallisation, as both appear to have much the same solubility. After numerous modifications had been tried, we ultimately found the following method the most satisfactory.

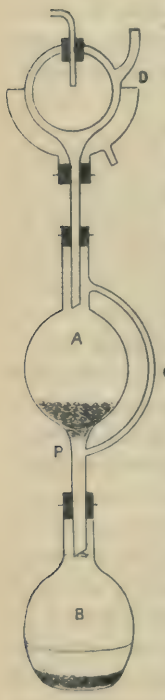
One hundred and fifty grams of calcium hydroxide are placed in a large open vessel capable of holding about 5 litres; half a litre of water is poured over the lime, a handful of ice and then 100 grams of furfural are added, the magma being thoroughly mixed by stirring. One hundred and ten grams of potassium permanganate, dissolved in 2 litres of water, are now added very slowly at first and more rapidly towards the end, vigorous stirring being maintained throughout the whole operation, which occupies about 30 minutes. Ice is added from time to time, the temperature being thus maintained at about 10°, and on no account being allowed to rise above 20°. The coffee-coloured liquid is now heated for a short time on a bath of boiling water to complete the reaction and facilitate the subsequent filtration. The whole is now filtered hot with the aid of a pump, the manganese sludge being washed with a little boiling water and well pressed with a spatula.

The filtrate, containing calcium hydroxide, and calcium and potassium pyromucates, is placed in a large evaporating basin and hydrochloric

acid added in sufficient quantity to just set free the whole of the pyromucic acid, congo-paper being used as an indicator of free mineral acid. The liquid is now evaporated on the water-bath until the crystals of pyromucic acid appearing around the edge are only with difficulty redissolved by the hot mother liquor. After rapid filtration, the hot liquid is set aside to cool, the pyromucic acid separating out in brown needles which are mixed with a little potassium chloride. These crystals, when filtered off and washed slightly, are pure enough for transformation into pyromucyl chloride by the process described below.

The mother liquor is repeatedly extracted with ether, the ethereal extracts dried over fused sodium sulphate, and the pyromucic acid obtained by evaporation as a brown liquid which solidifies on cooling to a yellowish, crystalline mass.

Fig. 1.



In this manner, from 100 grams of furfural 60—70 grams of pyromucic acid were obtained by crystallisation from the aqueous, and 10—20 grams from the ethereal liquid, or a yield of 70—80 grams altogether.

Preparation of Pyromucyl Chloride.—This was at first prepared from the acid by heating with phosphorus pentachloride to 100°, and distilling the acid chloride at atmospheric pressure (Liès-Bodart, *Annalen*, 1856, **100**, 325), but the yield by this method was extremely poor, most of the acid being apparently rapidly decomposed by the pentachloride.

Excellent results were, however, obtained by means of the following method, in which the phosphorus pentachloride is used in chloroform solution and is applied in an apparatus specially constructed for the purpose (Fig. 1).

In the flask (*B*) is placed about twice the quantity of phosphorus pentachloride theoretically required together with about 200 c.c. of pure dry chloroform; the pyromucic acid is placed in the bulb of the extraction apparatus (*A*), the lower extremity of which is plugged with glass wool, whilst the upper extremity is provided with a condenser (*D*) of the particularly compact type devised by one of us (*Chem. News*, 1899, **79**, 217). The flask (*B*) is heated by means of a water-bath, the manner in which the apparatus acts being obvious, and the heating is continued until the evolution of hydrogen chloride has almost ceased. Any mineral matter (potassium chloride) with which the pyromucic acid may be mixed remains on the glass wool plug owing to its insolubility in the chloroform.

After the reaction is complete (about 6 hours), the chloroform is

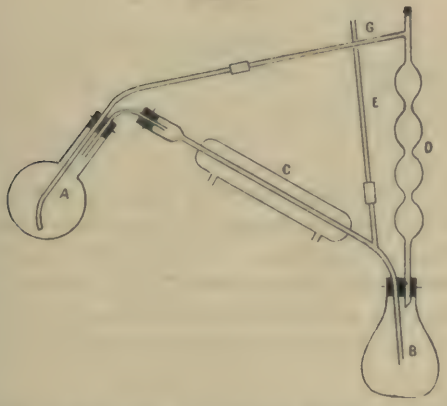
distilled off on the water-bath from the flask (*B*), the residue left being then poured into a fractionating flask and submitted to vacuum distillation. Nearly all the phosphorus oxychloride passes over below 45° under 10 mm. pressure, the receiver being then changed and all the distillate which will come off when the flask is heated in a bath of boiling water is collected. This is refractionated to get rid of phosphorus oxychloride. The boiling point of pure pyromucyl chloride is 66° under 10 mm. pressure; it is a colourless, strongly refracting liquid, rapidly decomposing in strong light, and its vapour has an extremely irritating effect on the eyes. It is almost unacted on by cold water and even with boiling water the action is very slow, much slower than in the case of benzoyl chloride and water.

This method gives a practically quantitative yield of pyromucyl chloride.

New Automatic Method for Preparation of Esters of Tartaric and other Non-volatile Acids.

We have found the following method of great advantage in preparing dimethyl and diethyl tartrates, and it may doubtless be of much wider utility. The arrangement of the apparatus will be sufficiently obvious from the accompanying sketch (Fig. 2).

FIG. 2.



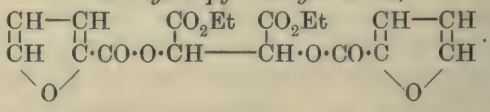
In the flask (*A*) are placed 100—200 grams of the acid (it need neither be specially dried nor powdered), which is then just covered with the alcohol. In the flask (*B*) is placed about one and a-half times as much of the alcohol as is required for the esterification of the whole of the acid taken; this flask (*B*) also contains a quantity of solid desiccating agent (we have always employed fused potassium carbonate). The whole apparatus forms a closed system which only com-

municates with the outer air through the open end (G) of the tube (E) which is fitted to the lower extremity of the condenser tube.

The flask (A) is immersed up to the neck in an oil-bath which is slowly heated to 130°, and as soon as most of the alcohol in (A) has distilled through the condenser (C) into (B), the latter is placed in a water-bath which is heated to boiling. The vapour from the boiling alcohol in (B) passes up the fractionating column (D) and bubbles through the mixture of acid and alcohol in (A), whilst the water formed in the esterification process passes along with alcohol vapour from (A) through the condenser and to the bottom of (B), where it is absorbed by the dehydrating agent. The interposition of the fractionating column (D) of course assists in the dehydration of the alcohol vapour passing from (B) to (A). Owing to the rigidity of the apparatus, a single clamp (not shown in the figure) on the condenser is sufficient for the support of the whole.

For the esterification of the quantity of tartaric acid by means of methyl or ethyl alcohol as indicated above, we have found that about 10 hours are requisite, and the operation can be temporarily interrupted at any time. The mixture of alcohol and ester in (A) is finally poured into a fractionating flask, and the two separated by vacuum distillation. Excellent yields amounting to 70—80 per cent. of the calculated quantity were thus obtained in the case of dimethyl and diethyl tartrates.

Diethyl Dipyromucyltartrate,



Thirty grams of diethyl tartrate and 75 grams of pyromucyl chloride (free from phosphorus oxychloride) were placed in a flask provided with a reflux air condenser, to the open upper extremity of which a calcium chloride tube was attached. The mixture was heated by means of an oil-bath to 155°, at which temperature reaction, accompanied by evolution of hydrogen chloride, took place. The temperature was finally raised to and maintained at 160—170° until this gas ceased to be evolved. Much decomposition had apparently taken place as a quantity of tarry matter was visible. On cooling overnight crystals separated out, which when filtered off were found to dissolve in a dilute solution of sodium carbonate, and were evidently pyromucic acid. The filtrate (a dark treacle) was dissolved in ether (chloroform was also sometimes used) and agitated for a day and a half with a solution of sodium carbonate on a shaking machine. The ether solution was then separated, dried with fused sodium sulphate, and

evaporated. The residue, which smelt very faintly of pyromucyl chloride, was dissolved in methylated spirit and decolorised by boiling with animal charcoal. The alcohol was distilled off and the residue poured into a dish and placed in a vacuum desiccator to crystallise. After drying the crystals on a porous plate, the yield of crude product did not amount to more than 10 grams. This was recrystallised from carbon disulphide until the melting point, 76°, was constant; the crystals were colourless, odourless, very soluble in alcohol or ether, a little less so in chloroform, benzene, or carbon disulphide, and quite insoluble in light petroleum. From a chloroform solution, on slow evaporation, the ester separated in long, flat plates over half an inch in length.

0·2203 gave 0·4435 CO_2 and 0·0975 H_2O. C = 54·90; H = 4·92.

$C_{18}H_{18}O_{10}$ requires C = 54·82; H = 4·57 per cent.

The substance could not be maintained in the liquid state below its melting point, hence all the density and polarimetric determinations were made above 76°.

d 99·5°/4° = 1·1914; 109·5°/4° = 1·1831; 140°/4° = 1·1524.

Rotation of diethyl dipyromucyltartrate.

Temp.	α_D. $l = 0·4991$.	α_D. $l = 1$.	$[\alpha]_D$.	$[M]_D$.
99·5°	−40·23°	−80·60°	−67·65°	−266·54°
109·5	−39·22	−78·58	−66·42	−261·69
140	−34·83	−69·78	−60·55	−238·57
[20	(calculated)		−81·56	−321·44]

The values for the specific rotation at the three observed temperatures, when plotted on a rotation-temperature diagram, lie practically on a straight line, and the value for 20° has therefore been calculated on the assumption that the influence of temperature on the rotation is uniform.

Rotation of diethyl dipyromucyltartrate in ethyl alcohol solution.
($l = 2·998$ *dcm.*)

Weight of solution, grams.	Weight of substance, gram.	Grams substances in 100 grams solution.	d 20°/4°.	$\alpha_D^{20°}$.	$-[\alpha]_D^{20°}$.	$[M]_D^{20°}$.
10·2325	0·0515	0·503	0·7939	−1·18°	−98·54°	−388·2
10·2561	0·1191	1·161	0·7966	−2·43	−87·62	−345·2
8·7215	0·1700	1·949	0·7993	−3·97	−85·00	−334·9
17·5542	0·5140	2·928	0·8004	−6·09	−86·66	−341·4
10·5345	0·5200	4·936	0·8078	−10·38	−86·82	−342·1

Thus the specific rotation in alcoholic solution at first very rapidly diminishes with increase in concentration from 0·50 to 1·16 per cent., after which, to 4·94 per cent., it remains practically constant. The rotation at higher concentrations could not be investigated owing to the limited solubility of the compound. The rotation in alcoholic solution, from 1·95 to 4·94 per cent., approximates closely to the rotatory power of the liquid compound calculated for 20° ($[\alpha]_D^{20°}$ −81·56°).

Dimethyl Dipyromucyltartrate.

Dimethyl dipyromucyltartrate was prepared in the same way as the ethyl ester. It was crystallised from carbon disulphide until of constant melting point 131°.

0·3322 gave 0·6385 CO_2 and 0·1178 H_2O. C = 52·41 ; H = 3·94.
$C_{16}H_{14}O_{10}$ requires C = 52·46 ; H = 3·83 per cent.

Molecular volume of diethyl dipyromucyltartrate.

Taking d 15°/4° = 1·2728.

$$\text{Mol. vol.} = \frac{394}{1{\cdot}2728} = 309{\cdot}5.$$

Calculated from Traube's formula (*Ber.*, 1895, **28**, 2724, 2924):

$C_{18} = 9{\cdot}9 \times 18 = 178{\cdot}2$; $H_{18} = 3{\cdot}1 \times 18 = 55{\cdot}8$; $O_{10} = 5{\cdot}5 \times 10 = 55$; Co-volume = 25·9 ; mol. vol. = 314·9.

For compounds containing an ethylene linking, Traube deducts 1·7 ; for a hexamethylene ring, 8·1 ; for a benzene ring, 13·2 (that is, 8·1 for the 6-carbon ring, and $3 \times 1{\cdot}7 = 5{\cdot}1$ for the three ethylene unions). The influence of the furfuran ring on molecular volume has not yet been determined.

We beg to express our thanks to the Government Grant Committee of the Royal Society for funds placed at our disposal.

The University,
Birmingham.

LVI.—*Formation of Amides from Aldehydes.*

By Robert Howson Pickard, D.Sc., Ph.D., and William Carter.

In general, the oxidation of an aldehyde in the presence of ammonia leads to the formation of the amide of the corresponding acid. Thus, when benzaldehyde is suspended in water, and oxidised with ammonium

persulphate in the presence of lime, with potassium persulphate in the presence of lime and ammonia, with ammonium persulphate in the presence of ammonia, with potassium permanganate in the presence of ammonia and lime, or with hydrogen peroxide in the presence of ammonia, varying yields of benzamide are obtained.

The procedure best adapted for the preparation of amides in this manner is as follows. The aldehyde dissolved or suspended in water is shaken with a slight excess of ammonium persulphate and the quantity of lime required to neutralise the acid set free on the reduction of the persulphate, and also to liberate the ammonia from the ammonium salts; the mixture is heated at 70° for half an hour (care being taken to avoid the very violent reaction, which sets in at 80°) and then filtered, the residue being washed with dilute ammonia to ensure the complete solution of the amide. When cool, the filtrate is acidified with hydrochloric acid, to decompose any additive or condensation compound of the aldehyde with ammonia, and extracted with ether; after washing the ethereal solution with a solution of sodium bisulphite, and then with sodium carbonate solution, the amide is obtained on evaporation of the ether. The yield of amide amounts to 30—40 per cent. of the weight of aldehyde taken. Only a small proportion of the aldehyde is oxidised to the corresponding acid, and the remainder can be recovered from the bisulphite solution and the residue left on filtration. By a repetition of the process, the yield of amide can be increased to 50—70 per cent. of the weight of aldehyde taken.

The following aldehydes and alcohols, when treated in this manner, yield the corresponding amides:—benzaldehyde, *m*- and *p*-nitrobenzaldehydes, anisaldehyde, acetaldehyde,* propylaldehyde, *i*-valeraldehyde and benzyl, ethyl, and *n*-propyl alcohols. Hydrobenzamide and acetaldehyde-ammonia, when oxidised with potassium persulphate in the presence of lime, yield respectively benzamide and acetamide. We did not succeed in obtaining any appreciable yield of the amides from the following:—*o*- and *p*-hydroxybenzaldehydes, furfuraldehyde, and cinnamaldehyde. This method also lends itself to the preparation of alkyl-substituted amides; thus, when benzaldehyde is oxidised with potassium persulphate in the presence of lime and methylamine or ethylamine, a good yield of benzoylmethylamine or benzoylethylamine is obtained.

The formation of amides in this manner is probably due to the direct oxidation of the additive compounds of the aldehydes with ammonia, that is, $R\cdot CH(OH)\cdot NH_2$ is oxidised to $R\cdot CO\cdot NH_2$, the group $:CH\cdot OH$ being as a rule easily oxidised to the group $:CO$.

* The method given has to be slightly varied in the case of acetamide, owing to the slight solubility of this substance in ether.

We wish here to express our thanks to the Research Fund Committee of the Birmingham Natural History and Philosophical Society, who have kindly provided some of the materials for this work.

MUNICIPAL TECHNICAL SCHOOL,
BLACKBURN.

LVII.—*Additive Compounds of α- and β-Naphthylamine with Trinitro-derivatives of Benzene.*

BY JOHN J. SUDBOROUGH.

IN a previous communication (Trans., 1899, **75**, 588), it was stated that when α-naphthylammonium 2 : 4 : 6-trinitrobenzoate is boiled with alcohol, the solution turns deep red, and on cooling, deposits deep brick-red needles.

This reaction has since been further studied, and it has been proved that the red substance is a direct additive compound of α-naphthylamine with *s*-trinitrobenzene, $C_{10}H_7{\cdot}NH_2,C_6H_3(NO_2)_3$, and that it is produced by the elimination of carbon dioxide from the trinitrobenzoate.

The same compound is also readily formed (1) by direct union of its constituents in alcoholic or benzene solution, (2) when α-naphthylammonium trinitrobenzoate is carefully heated in an oil-bath at 145—150°, (3), when α-naphthylamine hydrochloride and trinitrobenzene are boiled for some time with water. The compound is not produced, however, when a benzene solution of α-naphthylammonium trinitrobenzoate is boiled for several hours, in fact it appears that only those solvents which eliminate carbon dioxide from the free acid (compare Lepsius, *Ber.*, 1894, **27**, 1635) are capable of converting α-naphthylammonium trinitrobenzoate into the red compound. Only a minute quantity of the red crystals is obtained when an alcoholic solution of α-naphthylamine sulphate is boiled with trinitrobenzene.

In composition, the red compound resembles the additive compounds obtained by Hepp (*Annalen*, 1882, **215**, 344) from organic bases such as aniline, *o*-toluidine, &c., with trinitrobenzene. As regards properties, however, there appears to be a marked difference between them. Hepp describes his products, which also have a bright red colour, as extremely unstable molecular compounds, which are resolved into their constituents (*a*) when crystallised from alcohol, (*b*) when gently warmed, and (*c*) when left exposed to the air. He also states that they are instantaneously decomposed when treated with cold dilute mineral acids. All these observations I am able to confirm. α-Naphthylamine trinitro-

benzene, on the other hand, is an extremely stable substance; it may be repeatedly crystallised from alcohol or benzene, or even from glacial acetic acid, without undergoing resolution into its constituents. It may be left exposed to the atmosphere at the ordinary temperature for months without losing in weight or changing in appearance, and even when heated at 100° does not change in colour, although it gradually loses in weight. Dilute mineral acids act on it slowly in the cold, and the characteristic red colour gradually disappears; the decomposition is accelerated by heating the mixture to boiling, but if the colourless crystals which separate on cooling are removed, and then washed with a little cold water, the bright red colour is restored. Boiling hydrochloric acid appears to decompose the red compound into trinitrobenzene and α-naphthylamine hydrochloride, as the calculated amount of trinitrobenzene is obtained when the products of decomposition are extracted with ether. The fact that the products of decomposition turn red when collected and washed with cold water proves that even under these conditions the red compound can be produced from trinitrobenzene and α-naphthylamine hydrochloride.

The following compounds have also been prepared and examined: β-Naphthylamine trinitrobenzene, α- and β-naphthylamine trinitrotoluene, α- and β-naphthylamine ethyl trinitrobenzoate, α-naphthylamine methyl picrate, α-naphthylamine ethyl picrate, α- and β-naphthylamine picramide. All these compounds are derived from symmetrical trinitro-derivatives; so far, experiments have not been undertaken with other than symmetrical nitro-compounds, and, according to Hepp, isomeric trinitro-benzenes and -toluenes do not combine with aniline. Quite recently, however (*Ber.*, 1900, **33**, 2507), Reverdin and Crepieux have described a compound of α-naphthylamine with 3-chloro-4 : 6-dinitrotoluene which crystallises in orange needles melting at 98°. *s*-Trinitro-*m*-xylene and trinitromesitylene appear to be incapable of combining with organic bases.

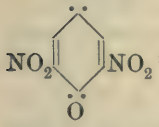
In certain respects these red compounds recall the metallic derivatives of trinitrobenzene, ethyl trinitrobenzoate, &c., described by Lobry de Bruyn (*Rec. Trav. Chim.*, 1895, **14**, 89, 150; 1896, **15**, 848); Loring Jackson (*Amer. Chem. J.*, 1897, **19**, 199; *Proc. Amer. Acad.*, 1898, **33**, 173; 1900, **35**, 263); V. Meyer (*Ber.*, 1894, **27**, 3153; 1896, **29**, 848), and Hantzsch and Kissel (*Ber.*, 1899, **32**, 3137).

With regard to the constitution of these compounds, it appears to be highly improbable that they can be "molecular compounds," such as Hepp considers his products to be. Of the many constitutional formulæ which suggest themselves, the following are the simplest:

(1) According to Bruni and Berti (*Chem. Centr.*, 1900, ii, 532), nitro-derivatives which contain a hydrogen atom in the ortho-position relatively to a nitro-group undergo more or less dissociation in formic

acid solution; trinitrobenzene would therefore appear to have acid properties and might combine with amines to form salts of the ammonium type, for example, $C_{10}H_7\cdot NH_2<^{H}_{C_6H_2(NO_2)_3}$.

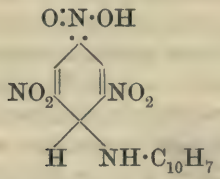
(2) The trinitrobenzene molecule might react in the tautomeric form,



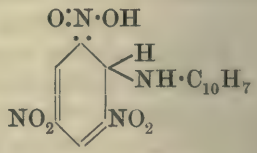
, as a dinitro-derivative of quinonemonoxime and form salts by the addition of an amine to the hydroxyl group.

(3) The addition of the amine may take place by the conversion of a $O{:}\dot{N}{:}O$ group into a $O{:}\dot{N}<^{OH}_{NH\cdot C_{10}H_7}$ group in the same way as that in which Hantzsch and Kissel consider that sodium ethoxide is added on to a nitro-group (*loc. cit.*).

(4) The red compounds may have a quinonoid structure resembling that attributed by Loring Jackson to the compounds of trinitroanisole and sodium ethoxide:



or



The formulæ 1 and 2 may be regarded as highly improbable, as the compounds do not appear to be salts of amines. They are far too stable in the presence of acids for this to be the case, and arylamines like 2:4 and 2:6-dibromoanilines, which do not yield salts with strong organic acids, readily form additive compounds with trinitrobenzene. Against constitution 1 may also be urged the fact that trinitrobenzene is not a sufficiently strong acid to have any of its hydrogen directly replaced when treated with metallic sodium (compare Lobry de Bruyn, *loc. cit.*), and therefore would not be likely to form salts with amines. As an additional argument against constitution 2 we have the fact that quinonemonoxime itself does not appear to combine with amines.

As formula 3 or 4 was considered to be probable, and each contains a free hydroxyl group, the action of acetic anhydride and of alcoholic potash on α-naphthylamine trinitrobenzene was investigated in order to determine whether definite acetyl or metallic derivatives could be isolated. Acetic anhydride readily reacts with the red compound, destroying the characteristic colour and leaving a yellow product, which crystallises from alcohol in sulphur-yellow needles

melting at 140·5°. This proved to be a monoacetyl derivative, $C_{10}H_{11}O_6N_4Ac$, but it contains the acetyl attached to nitrogen and not to oxygen, as identically the same product is formed when a mixture of molecular quantities of trinitrobenzene and acet-α-naphthalide is crystallised from alcohol. Further proof that it has this structure is afforded by the action of a methyl alcoholic solution of potassium hydroxide, which decomposes it into acet-α-naphthalide and a potassium derivative of trinitrobenzene.

As it was possible that this monoacetyl compound also contained a hydroxyl group, $(NO_2)_2C_6H_3\cdot N\begin{matrix}OH\\ \diagdown\\ \diagup\\ O\end{matrix}NAc\cdot C_{10}H_7$, the further action of acetic anhydride on the red compound and also on its monoacetyl derivative has been studied. The products formed, however, are trinitrobenzene, diacet-α-naphthalide, and a small amount of the monoacetyl derivative, thus indicating that the prolonged action of acetic anhydride decomposed the monoacetyl compound into trinitrobenzene and acet-α-naphthalide, which is then converted into diacetyl-α-naphthylamine (compare following paper). The action of a methyl alcoholic solution of potassium hydroxide has also been studied, but so far no well-defined metallic derivatives have been isolated. The products obtained from α-naphthylamine trinitrobenzene and β-naphthylamine trinitrobenzene contain amounts of potassium varying from 9—16 per cent., and are apparently mixtures. These reactions will be further investigated at lower temperatures.

At this stage of the work it is impossible to decide definitely between formulæ 3 and 4, and further experiments are in contemplation, which it is hoped may throw light upon this question.

Experimental.

α-Naphthylamine Trinitrobenzene, $C_6H_3(NO_2)_3,C_{10}H_7\cdot NH_2$.

This compound may obtained by the following methods.

1. *From* s-*Trinitrobenzoic Acid.*—Molecular quantities of the acid and of α-naphthylamine are separately dissolved in alcohol and the solutions mixed, when a copious white precipitate of α-naphthylammonium trinitrobenzoate is obtained. A further quantity of alcohol is added and the whole boiled in a reflux apparatus for about an hour; the liquid turns deep red and all the colourless salt gradually goes into solution. When allowed to cool, deep brick-red, glistening, prismatic needles are deposited from the solution, and a further quantity of these may be obtained from the mother liquor, the yield being about 90 per cent. of the theoretical.

The same compound is formed in small quantity by boiling the

trinitrobenzoate with water. It may be readily obtained by carefully heating the trinitrobenzoate in a test tube in an oil-bath at 145°; the colourless salt gradually assumes a pink tint and carbon dioxide is slowly evolved. If the temperature is kept at 145—150°, the reaction is complete in about 2 hours, and the yield is practically theoretical. The compound is pure after one crystallisation from benzene.

In this method of preparation, it is essential that the temperature should be carefully regulated, as if it is allowed to rise much above 150°, the whole mass melts after some time and nothing but a black, tarry mass is obtained.

2. *From Trinitrobenzene.*—One of the simplest methods for the preparation of the red compound is by the crystallisation of a mixture of molecular proportions of *s*-trinitrobenzene and α-naphthylamine from either boiling alcohol or benzene.

When equivalent quantities of trinitrobenzene and α-naphthylamine sulphate are boiled in alcoholic solution, the liquid turns deep red, but even after boiling for half an hour the greater part (80 per cent.) of the trinitrobenzene separates on cooling.

α-Naphthylamine trinitrobenzene forms well-developed, brick-red, glistening prisms melting at 214° to a deep red liquid. It dissolves readily in the following solvents when hot:—acetone, chloroform, benzene, alcohol, or glacial acetic acid, and is deposited unaltered from most solvents, on cooling, as brick-red, prismatic needles, but from benzene as glistening, red plates, and from acetone as well-developed, ruby-red prisms. It dissolves but sparingly in light petroleum (b. p. 100—110°), moderately in ether, and is practically insoluble in water or carbon disulphide. On analysis:

0·196 gave 27·2 c.c. nitrogen at 12° and 730 mm. N = 15·8.
0·5 „ 0·3 trinitrobenzene * (m. p. 121°) = 60.
$C_{16}H_{12}O_6N_4$ requires N = 15·7; trinitrobenzene = 59·9 per cent.

α-Naphthylamine trinitrobenzene is much more stable than aniline trinitrobenzene (*loc. cit.*), or the compounds of trinitrobenzene with substituted anilines. Comparative experiments have been made by exposing *o*-toluidine trinitrobenzene, which crystallises in bright red needles melting at 126°, and α-naphthylamine trinitrobenzene to atmospheric influences at the ordinary temperature for several weeks. The naphthylamine derivative does not alter in weight in the least when

* Estimation of trinitrobenzene. A given weight of the substance was boiled for a few minutes with dilute hydrochloric acid, and then extracted four times with ether; it was found necessary to shake thoroughly and to add sufficient water to dissolve the α-naphthylamine hydrochloride. If some of the precipitate remained undissolved, the percentage of trinitrobenzene usually was too low and the precipitate when collected and washed with water turned deep red, indicating the presence of trinitrobenzene.

left exposed for 2 months, and even when heated in a steam oven at 100° it loses in weight only gradually and does not change colour.

0·5 gram,					
after	5·5	12·5	30	44	68 hours,
lost	0·0032	0·0087	0·0170	0·0228	0·0344 gram.

The *o*-toluidine compound however, loses in weight even at the ordinary temperature, and after several months is completely converted into colourless crystals of trinitrobenzene melting at 121°.

0·25 gram,								
after	3	5	22	29	43	57	69	82 days,
lost	0·0014	0·0022	0·0065	0·0090	0·0140	0·020	0·025	0·033 gram.

Solutions of α-naphthylamine trinitrobenzene in different solvents differ in colour, the shades varying from a deep blood red in acetone to a reddish-yellow in acetic acid. The intensity of the colour diminishes rapidly as the solutions are diluted. The compound may be crystallised from hot glacial acetic acid, in which it is readily soluble, without undergoing decomposition. The addition of water to a very dilute solution in acetic acid precipitates the unaltered compound in the form of a bright red precipitate.

Mineral acids decompose it but slowly in the cold, rapidly on warming, and, as already stated, when the products of decomposition are washed with water they assume a bright red appearance, owing to the re-formation of a certain amount of the red compound.

Action of Acetic Anhydride.—A monoacetyl derivative, $C_{16}H_{11}O_6N_4Ac$, is readily obtained when the red crystals (2 grams) are heated for a minute or two with acetic anhydride (3 c.c.). The red colour disappears, and, when the resulting orange-yellow liquid is poured into water, a yellow precipitate is formed. This, when recrystallised from dilute alcohol, gives an almost theoretical yield of the monoacetyl derivative, which crystallises in long, hair-like needles of a sulphur-yellow colour, melts at 140·5°, is fairly readily soluble in the usual organic solvents, and may be crystallised from acetic acid without decomposition. On analysis:

0·198 gave 24·3 c.c. nitrogen at 16° and 760 mm. N = 14·3.
0·5 „ 0·269 trinitrobenzene (m. p. 121°) = 53·8.
$C_{18}H_{14}O_7N_4$ requires N = 14·1; trinitrobenzene = 53·6 per cent.

As dilute hydrochloric acid does not appear to decompose the acetyl derivative in the cold, the compound was boiled with it for an hour; complete solution took place, and from the clear, colourless liquid, which had a strong odour of acetic acid, crystals of trinitrobenzene together with a little α-naphthylamine hydrochloride were deposited

on cooling. The whole was extracted four times with ether, the ethereal solution dried over calcium chloride, and the ether slowly evaporated from a tared flask.

The same acetyl derivative is formed when a mixture of trinitrobenzene and acet-α-naphthalide is crystallised from alcohol. Its melting point, 140·5°, was not lowered when the substance was mixed with the product just described. The acetyl group in the monoacetyl derivative is therefore, presumably, attached to nitrogen.

α-Naphthylamine trinitrobenzene, when boiled with an excess of acetic anhydride for an hour, does not yield a diacetyl derivative, but gives a mixture of the yellow needles of the monoacetyl derivative melting at 140·5°, of colourless plates of trinitrobenzene melting at 121°, and of well-developed, hard, rhomboidal prisms of diacetyl-α-naphthylamine, which, after crystallisation from alcohol, melt at 130° (compare following paper). On analysis:

0·403 gave 20·6 c.c. nitrogen at 12° and 762 mm. N = 6·08.

$C_{14}H_{13}O_2N$ requires N = 6·16 per cent.

When a cold methyl alcoholic solution of potassium hydroxide (1 mol.) is slowly added to a benzene solution of the monoacetyl derivative, a deep red precipitate is formed, which, after washing with warm benzene, is found to contain 13·3 per cent. of potassium, and the benzene filtrate gives colourless crystals which, after one crystallisation, melt at 159°. Methyl alcoholic potash thus converts the monoacetyl derivative into Lobry de Bruyn's potassium derivative of trinitrobenzene, $C_6H_3(NO_2)_3$,KOMe,$\frac{1}{2}H_2O$ (K = 13·3 per cent.), and acet-α-naphthalide.

The action of methyl alcoholic potash on α-naphthylamine trinitrobenzene has also been studied. As the red crystals are so sparingly soluble in cold organic solvents, they were finely ground, moistened with a little methyl alcohol, and then treated with the alcoholic potash (1 mol.); a red, crystalline product was obtained, which, after washing with warm benzene, was found to contain in different specimens 11·25, 12·93, and 13·2 per cent. of potassium.

β-Naphthylamine Trinitrobenzene.

This compound has been prepared by methods exactly similar to those used for the α-compound.

(1) Boiling β-naphthylammonium trinitrobenzoate (Trans., 1899, **75**, 588) with alcohol. As the product is more readily soluble in alcohol than the isomeric α-compound, it is not necessary to use so large a volume of alcohol. As the solution cools, β-naphthylamine trinitrobenzene is deposited in the form of deep red, lustrous needles.

(2) When the trinitrobenzoate is carefully heated in an oil-bath, carbon dioxide begins to be evolved at 135°, and the reaction is complete after about 2 hours' heating at 145°.

(3) When a mixture of β-naphthylamine and *s*-trinitrobenzene in molecular proportion is crystallised from benzene or alcohol, the yield of the compound is practically theoretical.

(4) When a mixture of trinitrobenzene (0·5 gram) and β-naphthylamine hydrochloride (0·45 gram) is boiled for half an hour with water (50 c.c.); even in the cold the hydrochloride turns a deep red colour. The yield amounts to 70 per cent. of the theoretical.

β-Naphthylamine trinitrobenzene crystallises in deep brick-red, prismatic needles, in appearance very similar to the α-compound. It melts at 162° and is more readily soluble than its isomeride in most organic solvents, including hot carbon disulphide or light petroleum (b. p. 100—110°). It may be recrystallised from acetic acid without undergoing decomposition, and may also be left exposed to the atmosphere at the ordinary temperature for several months without losing in weight or altering in appearance. On analysis:

0·2 gave 28 c.c. nitrogen at 17° and 735 mm. N = 15·7.
0·5 ,, 0·3004 trinitrobenzene (m. p. 121°) = 60·08.
$C_{16}H_{12}O_6N_4$ requires N = 15·7; trinitrobenzene = 59·9 per cent.

According to Loring Jackson and Gazzolo (*Proc. Amer. Acad.*, 1900, **35**, 263), trinitrobenzene and similar compounds are capable of combining with 3 mols. of sodium ethoxide, ethyl sodiomalonate, &c.; with amines, however, they appear to be capable of combining with only 1 mol., as even when a mixture of trinitrobenzene (1 mol.) and β-naphthylamine (2 mols.) is crystallised from benzene, the substances isolated are the compound, $C_6H_3(NO_2)_3,C_{10}H_7\cdot NH_2$, melting at 162° and unaltered β-naphthylamine.

Acetyl Derivative.—When the red crystals (2 grams) are left in contact with acetic anhydride (3 c.c.) for a few minutes, the mixture becomes quite hot, the red colour disappears, and an orange mass of the monoacetyl derivative is obtained. The reaction between the β-compound and acetic anhydride takes place more readily than is the case with the α-compound, and does not need the application of external heat to complete it. The acetyl derivative, $C_{16}H_{11}O_6N_4Ac$, crystallises from alcohol in sulphur-yellow, hair-like needles exactly resembling the acetyl derivative of the α-compound. It melts at 142°, and in solubility and general properties resembles the α-isomeride. The melting points are also very close together, but a mixture of the α- (m. p. 140·5°) and β- (m. p. 142°) compounds begins to melt at 130°. On analysis:

0·201 gave 24·6 c.c. nitrogen at 13° and 750 mm. N = 14·27.
0·5 ,, 0·2675 trinitrobenzene (m. p. 121°) = 53·5.
$C_{18}H_{14}O_6N_4$ requires N = 14·1 ; trinitrobenzene = 53·6 per cent.

Identically the same acetyl derivative is formed when a mixture of acet-β-naphthalide and trinitrobenzene in molecular proportion is crystallised from dilute alcohol.

When β-naphthylamine trinitrobenzene is treated with acetyl chloride, the red colour is immediately destroyed, a vigorous action results, and when the product is poured into water and crystallised from alcohol, colourless plates of trinitrobenzene melting at 121° are obtained. The prolonged action of acetic anhydride also decomposes the red crystals, and among the products formed are the monoacetyl derivative, acet-β-naphthalide, trinitrobenzene, and a dark coloured substance.

α-Naphthylamine Trinitrotoluene.

Equivalent quantities of α-naphthylamine and trinitrotoluene are separately dissolved in alcohol and the solutions then mixed ; as the solution cools, long, dark red, prismatic needles melting at 141·5° separate. The yield is practically theoretical, and the different fractions all melt at the same temperature. On analysis :

0·22 gave 29·4 c.c. of nitrogen at 18° and 737 mm. N = 15·0.
0·528 ,, 0·322 trinitrotoluene (m. p. 81°) = 61.
$C_{17}H_{14}O_6N_4$ requires N = 15·1 ; trinitrotoluene = 61·4 per cent.

α-Naphthylamine trinitrotoluene dissolves readily in most organic solvents, is only sparingly soluble in light petroleum (b. p. 100°), and the solution is pale yellow in colour, although on cooling dark red needles are obtained. The chloroform solution is deep red and deposits red prisms on cooling.

A definite compound of trinitrotoluene and acet-α-naphthalide has so far not been isolated ; when equivalent quantities of the constituents are crystallised from benzene or alcohol, the naphthalide crystallises unaltered, and even when a large excess of trinitrotoluene is used colourless crystals of the acet-α-naphthalide are formed ; when acetone is employed as the solvent and a large excess of trinitrotoluene is employed, yellow needles are obtained, but when thees are washed with either acetone or benzene they become colourless, and after crystallisation from alcohol have the melting point of acet-α-naphthalide.

β-Naphthylamine Trinitrotoluene.

β-Naphthylamine trinitrotoluene forms bright red, prismatic needles lighter in colour than the α-compound. It melts at 113·5° and is

readily soluble in most organic solvents, and moderately so in hot carbon disulphide or light petroleum. On analysis:

0·2125 gave 28·2 c.c. nitrogen at 14° and 737 mm. N = 15·1.
0·5100 ,, 0·317 trinitrotoluene (m. p. 81°) = 62·1.
$C_{17}H_{14}O_6N_4$ requires N = 15·1; trinitrotoluene = 61·4 per cent.

Acetyl Derivative, $C_{17}H_{13}O_6N_4 \cdot CO \cdot CH_3$.—The acetyl derivative is best obtained when a mixture of acet-β-naphthalide and an excess of trinitrotoluene is crystallised from benzene or acetone. It separates in yellow needles melting at 106°, but when crystallised from much benzene or ethyl alcohol is partially converted into its constituents.

0·5 gave 0·2794 trinitrotoluene (m. p. 81°) = 55·9.
$C_{19}H_{16}O_7N_4$ requires trinitrotoluene = 55·0 per cent.

α-Naphthylamine Ethyl Trinitrobenzoate, $CO_2Et \cdot C_6H_2(NO_2)_3, C_{10}H_7 \cdot NH_2$.

This compound is obtained as deep prune coloured needles when hot alcoholic or benzene solutions of α-naphthylamine (0·5 gram) and ethyl trinitrobenzoate (1 gram) (compare Trans., 1895, 67, 600) are mixed and allowed to cool. It melts at 135—136°, is moderately soluble in carbon disulphide or light petroleum, and readily so in most other organic solvents. It is easily decomposed by acetic acid or mineral acids, and even when boiled with alcohol. On analysis:

0·208 gave 24·1 c.c. nitrogen at 18° and 749 mm. N = 13·18.
0·5068 ,, 0·332 ethyl trinitrobenzoate (m. p. 153°) = 65·5.
$C_{19}H_{16}O_8N_4$ requires N = 13·1; ethyl trinitrobenzoate = 66·6 per cent.

β-Naphthylamine Ethyl Trinitrobenzoate.

When a hot alcoholic solution of the two constituents is allowed to cool, crystals of ethyl trinitrobenzoate are first deposited, and then prune coloured needles, but if the hot solution is poured into water a purple precipitate is obtained. This melts at 127°, and when crystallised from a mixture of light petroleum and a little benzene is deposited in the form of long, hair-like needles of a deep prune colour which melt at 127°.

0·21 gave 24·3 c.c. nitrogen at 19° and 749 mm. N = 13·1.
0·3 ,, 0·203 ethyl trinitrobenzoate (m. p. 153°) = 67·6.
$C_{19}H_{16}O_8N_4$ requires N = 13·1; ethyl trinitrobenzoate = 66·6 per cent.

It is readily soluble in cold chloroform, benzene, or acetone, yielding prune coloured solutions. When dissolved in hot light petroleum, the colour fades to a considerable extent, but reappears on cooling, and

prune coloured needles are deposited. Glacial acetic acid and dilute hydrochloric acid instantaneously destroy the colour, and it does not reappear on the addition of water.

α-Naphthylamine Picramide, $NH_2 \cdot C_6H_2(NO_2)_3, C_{10}H_7 \cdot NH_2$.

This compound is formed when a mixture of equivalent quantities of the constituents is crystallised from benzene or alcohol. It forms deep purple, glistening, prismatic needles, melts at 203°, and is fairly readily soluble in most organic solvents, yielding purple solutions, but appears to be partially decomposed by hot carbon disulphide or glacial acetic acid, as these, on cooling, give mixtures of purple needles with yellow prisms melting at 188°. On analysis :

0·1564 gave 26·3 c.c. nitrogen at 18° and 739 mm. N = 18·9.
0·5047 „ 0·311 picramide = 61·6.
$C_{16}H_{13}O_6N_5$ requires N = 18·9 ; picramide = 61·4 per cent.

β-Naphthylamine Picramide.

This is readily obtained when a hot benzene solution of the constituents is allowed to cool. It forms hard, brilliant, prismatic purplish-black needles, and melts at 161·5°. On analysis :

0·15 gave 25·4 c.c. nitrogen at 19° and 737 mm. N = 18·9.
0·5 „ 0·3078 picramide = 61·6.

α-Naphthylamine Ethyl Picrate, $OEt \cdot C_6H_2(NO_2)_3, C_{10}H_7 \cdot NH_2$.

This compound is readily obtained when the constituents are dissolved in benzene and the solution diluted with light petroleum (b. p. 80—85°). It forms glistening, flat, brick-red needles, melts at 79·5°, and dissolves fairly readily in most organic solvents. It crystallises from light petroleum in pale red needles, but when dissolved in ethyl alcohol or acetic acid is decomposed into its constituents, as colourless crystals are obtained when these are diluted with water. It is fairly readily decolorised by dilute mineral acids. On analysis :

0·2125 gave 26·1 c.c. nitrogen at 19° and 751 mm. N = 13·95.
0·510 „ 0·321 ethyl picrate (m. p. 77°) = 63·0.
$C_{18}H_{16}O_7N_4$ requires N = 14 ; ethyl picrate = 64·2 per cent.

α-Naphthylamine Methyl Picrate.

This compound, obtained in a similar manner to the ethyl derivative, forms small, dark-red needles melting at 75°. On analysis :

0·2062 gave 26·0 c.c. nitrogen at 17° and 753 mm. N = 14·5.
0·5 „ 0·3144 methyl picrate = 62·9.
$C_{17}H_{14}O_7N_4$ requires N = 14·5; methyl picrate = 63 per cent.

It has been found impossible to isolate definite compounds of β-naphthylamine with either methyl or ethyl picrate. That such compounds are actually formed is shown by the deep red colour produced when solutions of the two constituents are mixed; the products, however, are too readily soluble in benzene to be isolated, and are decomposed when warmed with alcohol. A small quantity of bright red, glistening plates was obtained from β-naphthylamine and methyl picrate when warm light petroleum was employed, but the amount isolated was too small for analysis, the chief product being an orange-yellow, amorphous powder insoluble in light petroleum or in alcohol, and not melting at 220°.

It would appear that all the compounds derived from α- or β-naphthylamine and substituted trinitrobenzenes are less stable, and more readily decomposed into their constituents, than the compounds of the same bases with trinitrobenzene itself. The substituted trinitrobenzenes whose substituents are relatively small, (CH_3,NH_2), appear to yield more stable derivatives than those in which the substituents are larger.

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LVIII.—*Acetylation of Arylamines.*

By JOHN J. SUDBOROUGH.

IN the preceding communication (p. 528), it has been shown that when α-naphthylamine trinitrobenzene is warmed for a few minutes with an excess of acetic anhydride, a monoacetyl derivative, $C_6H_3(NO_2)_3$,$C_{10}H_7$·NHAc, is formed, but that when the heating is prolonged for an hour decomposition ensues, and the products are trinitrobenzene and diacetyl-α-naphthylamine. This result pointed to the remarkable readiness with which α-naphthylamine or its monoacetyl compound is converted into a diacetyl derivative, and it was considered advisable to try a few comparative experiments with α- and β-naphthylamines.

Some few years ago, Kay (*Ber.*, 1893, **26**, 2851) showed that diacetyl derivatives of aniline and *o*- and *p*-toluidine can be obtained

by the action of acetyl chloride on the monoacetyl compounds at a temperature of 180°. The following year, Bistrzyki and Ulffers (*Ber.*, 1894, **27**, 91) showed that acetic anhydride could be substituted for the chloride, and that if the temperature be raised to 200—205°, a 90 per cent. yield of the diacetyl compound may be obtained. About the same time, Ulffers and von Janson (*Ber.*, 1894, **27**, 93) investigated the action of acetic anhydride on a number of substituted anilines, mostly at fairly high temperatures, and concluded that acid substituents (Cl, Br, NO_2) in ortho-positions tend to retard the formation of a monoacetyl derivative, but that when the one acetyl group has been introduced the same ortho-substituents facilitate the formation of a diacetyl compound. Thus an arylamine, like *s*-tribromoaniline, which contains two bromine atoms in ortho-positions with respect to the amino-group, is practically not acted on by acetic anhydride in the cold, but when boiled with an excess of the anhydride for an hour, gives a good yield of the diacetyl derivative.

No experiments have been described with arylamines containing positive substituents. As the work undertaken with the naphthylamines indicated that the α-compound is more readily diacetylated than the isomeric β-compound (pp. 539, 540), it was decided to compare the behaviour of arylamines containing a methyl group in an ortho-position with that of arylamines free from an ortho-substituent. The bases selected were aniline, *o*- and *p*-toluidine, and ψ-cumidine, and the action of acetic anhydride on them and on their monoacetyl derivatives has been studied.

The arylamine (1 mol.) was boiled for an hour with acetic anhydride (4 mols.) in a flask fitted with an air condenser and calcium chloride tube. The conditions were, as far as possible, kept the same, and at the end of the given time the excess of acetic anhydride was distilled off under reduced pressure, and the mono- and di-acetyl derivatives separately isolated by fractional crystallisation or by distillation under reduced pressure. The results obtained indicate that a base with a methyl group in an ortho-position, as in *o*-toluidine and ψ-cumidine, gives a better yield of diacetyl derivative than one in which an ortho-substituent is not present.

When the monoacetyl derivatives were employed, 1 mol. was boiled for an hour with 2 mols. of acetic anhydride, and the product then treated as in the previous cases. The results obtained were very similar to those given by the bases themselves.

These results, taken in conjunction with those of Ulffers and von Janson, indicate that a substituent, whether of positive or negative character in the ortho-position to an amino-group of a primary arylamine, facilitates the formation of a diacetyl derivative. The results obtained so far do not enable conclusions to be drawn as to the

differences in the accelerating actions of different substituents, but I hope shortly to be able to undertake experiments with the object of settling this point.

The experiments described in this paper establish beyond doubt that the ordinary arylamines are much more readily diacetylated than is generally believed ; for example, when aniline (1 mol.) and acetic anhydride (4 mols.) are boiled for an hour, 53 per cent. of the amine is converted into the diacetyl derivative, and other amines give even better yields.

The accelerating effect of ortho-substituents on diacetylation appears to be all the more remarkable when compared with previous work on di-ortho-substituted acids (*Ber.*, 1894, **27**, 510, 1580, 3146 ; Trans., 1895, **67**, 587, 601 ; 1897, **71**, 229), in which it has been shown that various reactions, most of which can be regarded as of an additive nature, are retarded by the presence of ortho-substituents. Emil Fischer too has shown (*Ber.*, 1900, **33**, 345, 1967) that the presence of ortho-substituents in a tertiary aromatic amine of the type



completely inhibits the formation of quaternary ammonium compounds.

Ulffers and von Janson's observations that ortho-substituents retard the formation of monoacetyl derivatives renders the subject even more complex, as these same groups facilitate the introduction of a second acetyl group.

One of the simplest explanations of the process of acetylation by the aid of acetic anhydride, refers the production of the acetyl derivative to the formation of an additive compound of the arylamine and anhydride, which subsequently decomposes into the monoacetyl derivative and acetic acid :

$$R{\cdot}NH_2 + Ac_2O = R{\cdot}NH_2{<}^{OAc}_{Ac} = R{\cdot}NHAc + HOAc.$$

The formation of a diacetyl compound may also be assumed to proceed in a similar manner,

$$R{\cdot}NAcH + Ac_2O = R{\cdot}NAcH{<}^{OAc}_{Ac} = R{\cdot}NAc_2 + HOAc.$$

If this actually represents the course of the reaction, then by analogy with other additive reactions the ortho-substituents would be expected to exert an inhibiting influence, whereas although they do seem to retard it to a certain extent in the first stage, they accelerate it in the second.

Are we to conclude that the processes of mono- and of di-acetylation are essentially different, or can a simple explanation be offered?

An explanation which presented itself to me, but for which at present absolutely no experimental proof can be produced, is as follows.

The additive products of the arylamines with acetic anhydride, the monoacetylarylamine acetates, will almost certainly be of varying degrees of stability, and as the diacetyl derivatives can only be formed after the decomposition of the additive compound, it would follow that the monoacetyl derivatives whose acetates are the least stable are most readily diacetylated.

It is a well-known fact that substituents in a succinic acid facilitate the removal of water and the formation of succinic anhydrides; in a similar manner, the ortho-substituent may facilitate the removal of acetic acid from the additive compound, and in this way accelerate the formation of a diacetyl derivative.

All attempts to isolate the additive compounds have proved fruitless.

When acetanilide is crystallised from glacial acetic acid, or from a mixture of acetic acid and chloroform, the unaltered anilide is obtained. Further, when *p*-toluidine (1 mol.) is mixed with acetic anhydride (1 mol.) in a vessel surrounded by ice, the product does not set to a solid mass of aceto-*p*-toluidide acetate, but has a pasty appearance, and a strong odour of acetic acid, and when kept over sulphuric acid for some time leaves the monoacetyl derivative.

Experimental.

Acetylation of Aniline.

Aniline (10 grams) was boiled for 1 hour with acetic anhydride (44 grams) and the excess of anhydride and acetic acid distilled off under reduced pressure, the distillation being continued until the temperature rapidly rose to about 120°. The residue in the flask was mixed with a little benzene, and, on cooling, crystals of acetanilide were deposited; a little light petroleum (b. p. 80—90°) was then added, when a further quantity of acetanilide was obtained. The mother liquor was evaporated, and the residue crystallised from a considerable amount of light petroleum (b. p. 40—50°), when the diacetyl derivative was obtained in the form of glistening plates melting at 37°. The small amount of residue, insoluble in light petroleum, gave, on crystallisation from benzene, a further quantity of acetanilide.

The amounts obtained were:

	Grams.	M. p.	Per cent.
Monoacetyl.....	5·6	114°	38·5
Diacetyl	10·0	37	53

Acetanilide (10 grams) and acetic anhydride (16 grams) were then

boiled for an hour, and the product treated in exactly the same manner as described above; the amounts obtained were:

	Grams.	M. p.	Per cent.
Monoacetyl.....	3·0	114°	30
Diacetyl	8·7	37	66

The melting point of diacetylaniline, as given by Kay (*loc. cit.*), is 37—37·5°.

Acetylation of o-*Toluidine.*

o-Toluidine (10 grams) and acetic anhydride (38 grams) were boiled together for an hour, the excess of acetic anhydride was distilled off under reduced pressure, a little benzene and light petroleum were added to the residue in the flask, when a small amount of monoacetyl derivative melting at 110° was obtained. The benzene and light petroleum were distilled off, and the residual oil distilled under diminished pressure; nearly the whole passed over at 152—153° under 20 mm. pressure, and only a slight residue remained in the flask. From the latter, a minute quantity of monoacetyl derivative was obtained. The diacetyl-*o*-toluidine, when kept for some time, deposited extremely well-developed pyramids melting at about 18°; Kay gives the boiling point as 150—151° under 16 mm. pressure, and Clayton (*Ber.*, 1895, **28**, 1665) the melting point as 18°.

The amounts obtained were:

	Grams.	M. p.	Per cent.
Monoacetyl.....	1	110°	7
Diacetyl	14·5	18	81

Ten grams of aceto-*o*-toluidide were boiled for an hour with 14 grams of acetic anhydride, and the product distilled under reduced pressure; 12 grams of oil distilling at 152—153° under 20 mm. pressure were obtained. The residue in the flask gave 0·25 gram of unaltered monoacetyl derivative.

Acetylation of p-*Toluidine.*

This was carried out in precisely the same manner as described for the ortho-compound. On the addition of benzene, after removal of the acetic anhydride, colourless crystals of the monoacetyl derivative, melting at 148—149°, were obtained. The mother liquor was distilled under reduced pressure, and 9·6 grams of an oil obtained which passed over at 167—168° under 22—23 mm. pressure. When cold, this set into a mass of colourless crystals melting at about 40°, and after recrystallisation from light petroleum at 48°. Kay gives the boiling point of diacetyl-*p*-toluidine as 160—161° under 15 mm. pressure, and Clayton the melting point as 48°. The quantities obtained were:

	Grams.	M. p.	Per cent.
Monoacetyl.....	4·5	149°	32·3
Diacetyl	10·7	47	60·0

An experiment was then made by heating aceto-*p*-toluidide (10 grams) with acetic anhydride (14 grams) for an hour. The products were separated as in the previous case, and the results obtained were :

	Grams.	M. p.	Per cent.
Monoacetyl.....	2·4	150°	24
Diacetyl	9·2	48	72

Acetylation of ψ-Cumidine, $C_6H_2Me_3{\cdot}NH_2$, $[NH_2 : Me_3 = 1 : 2 : 4 : 5]$.

Ten grams of the base and 30 grams of acetic anhydride were boiled for an hour, and the excess of anhydride distilled off under reduced pressure. The oily residue solidified on cooling, and was then extracted with warm light petroleum (b. p. 50—60°). The monoacetyl derivative was left behind in the form of a fine powder which, after recrystallisation from dilute alcohol, formed colourless needles melting at 161°.

The diacetyl compound, $C_6H_2Me_3{\cdot}NAc_2$, crystallised from the light petroleum in extremely well-defined, hard, transparent prisms, but usually mixed with a small amount of the monoacetyl compound, from which it was freed by recrystallisation. It melts at 59·5°, and is readily soluble in all the ordinary organic solvents, but insoluble in water. On analysis :

0·3908 gave 21·1 c.c. moist nitrogen at 15° and 768 mm. N = 6·4.

$C_{13}H_{17}O_2N$ requires N = 6·4 per cent.

0·2 gram was boiled with 50 c.c. of standard barium hydroxide solution (protected from atmospheric carbon dioxide) for a few minutes until all the oil had disappeared, and then titrated with standard sulphuric acid (1 c.c. = 0·0088 gram), using phenolphthalein as indicator ; 12·2 c.c. of the acid were required in one experiment, and 12·3 c.c. in a second. A blank experiment in which 50 c.c. of the barium hydroxide solution were boiled without the addition of the diacetyl compound required 17·3 c.c. of acid. Hence the amount of acetyl = 19·5, that calculated being 19·6 per cent., provided only one acetyl group is removed. The precipitate, consisting of barium sulphate and the product of hydrolysis, was extracted with dilute alcohol, and colourless needles of the monoacetyl derivative melting at 162° were obtained. Boiling with baryta water for a few minutes thus removes one of the acetyl groups, but leaves the other intact.

Shaking the diacetyl derivative with dilute sodium hydroxide solution has a similar action, but is somewhat more difficult to regulate,

owing to the fact that the compound clots together, and thus is not acted on by the alkali. Boiling with aqueous or alcoholic soda for several hours does not completely remove the two acetyl groups (compare Kay, *loc. cit.*).

The weights of mono- and di-acetyl derivatives obtained from 10 grams of the base were :

	Grams.	M. p.	Per cent.
Monoacetyl	1·3	161—162°	10
Diacetyl	13·7	59·5	85

An experiment was then made by heating the monoacetyl compound (10 grams) with acetic anhydride (12 grams) for an hour, and the product separated as before :

	Grams.	M. p.	Per cent.
Monoacetyl	0·8	161°	8
Diacetyl	11·0	59·5	89

Acetylation of α-Naphthylamine.

Ten grams of the base were boiled for an hour with 28·6 grams of acetic anhydride ; when cold, a considerable amount of well-defined, prismatic crystals separated. The excess of acetic anhydride was removed by distillation under reduced pressure, and the residue then fractionally crystallised from ethyl alcohol. The diacetyl derivative crystallises first in the form of well-developed, hard prisms ; these are followed by a mixture of mono- and di-acetyl derivatives, which may be separated mechanically as the monoacetyl compound crystallises in feathery needles and the diacetyl in fairly large prisms ; a small amount of the mixed acetyl derivatives is finally obtained, which could not be separated into its constituents. The amounts obtained were :

	Grams.	M. p.	Per cent.
Monoacetyl	1·9	159°	14·7
Diacetyl	11·9	130	75·0

Diacetyl-α-naphthylamine crystallises readily from most organic solvents. It is deposited from its alcoholic or benzene solutions in well-developed, slightly opaque, colourless crystals, having a striated structure somewhat resembling that of potassium iodide crystals. It melts at 130°, and loses one of its acetyl groups when boiled with aqueous alkalis. 0·3 gram was boiled for half an hour with 50 c.c. of standard barium hydroxide solution, and then required 10 c.c. of sulphuric acid (1 c.c. = 0·0088 gram) for neutralisation, using phenolphthalein as indicator. Fifty c.c. of the baryta water, when boiled alone in a similar manner, required 17·3 c.c. of sulphuric acid for neutralisation. Hence the amount of acetyl = 18·8, that calculated being 19·0 per cent. provided only one acetyl group is removed. Although there was a

slight odour of α-naphthylamine after boiling with the alkali, the product obtained was found to be acet-α-naphthalide, as when crystallised from dilute alcohol it melted at 159°.

On analysis of the diacetyl derivative, the following numbers were obtained:

0·4 gave 21·8 c.c. moist nitrogen at 12° and 755 mm. N = 6·4.
0·4079 „ 22·5 c.c. „ „ 14° „ 754 „ N = 6·4.
$C_{14}H_{13}O_2N$ requires N = 6·2 per cent.

Acetylation of β-Naphthylamine.

The acetylation of β-naphthylamine was performed in exactly the same manner as with the α-compound, and the excess of acetic anhydride removed by distillation under reduced pressure. The residue had a somewhat syrupy consistency, and did not crystallise at all readily; after trying several methods for the separation of the mono- and di-acetyl derivatives, the following was found to give the best results.

The syrupy residue was dissolved in slightly more than its own volume of benzene and the acet-β-naphthalide which crystallised out was collected on a filter; light petroleum was added, when a further quantity of the monoacetyl derivative was obtained. The clear filtrate, when left to evaporate spontaneously, gave a crust of the diacetyl compound on the sides of the beaker; as this did not crystallise well, the whole of the benzene and light petroleum was removed by evaporation and the residue crystallised from light petroleum (b. p. 50—60°), when the diacetyl derivative was obtained in the form of clusters of snow-white plates melting at 66·5°. When crystallised from benzene, the small amount of residue insoluble in light petroleum gave about 0·5 gram of the monoacetyl derivative. The numbers obtained were:

	Grams.	M. p.	Per cent.
Monoacetyl.....	5·5	133°	42·5
Diacetyl	7·7	66·5	48·5

Diacetyl-β-naphthylamine, $C_{10}H_7 \cdot NAc_2$, crystallises from light petroleum or from dilute alcohol in colourless plates melting at 66·5° and readily soluble in most organic solvents.

0·771 gave 40·9 c.c. nitrogen at 10° and 756 mm. N = 6·3.
0·4563 „ 24·9 c.c. „ 16° „ 740 „ N = 6·2.
$C_{14}H_{13}O_2N$ requires N = 6·2 per cent.

It appears to be less readily hydrolysed than the α-compound, as when boiled with excess of baryta water for an hour it was not completely decomposed into the monoacetyl derivative. 0·5 gram was

boiled in a reflux apparatus fitted with a soda-lime tube for an hour with 10 c.c. of methyl alcoholic potash, the solution then required 38·0 c.c. of sulphuric acid (1 c.c. = 0·0088 gram) for neutralisation, and as 10 c.c. of the original alcoholic potash required 50·3 c.c. of sulphuric acid, the amount of acetyl = 19·0, that calculated being 19·0 per cent. provided only one acetyl group is removed. The melting point of the product was 132·5°, proving it to be acet-β-naphthalide.

Acetylation of 2 : 6-Dibromoaniline.

A good yield of diacetyl-2 : 6-dibromoaniline, $C_6H_3Br_2{\cdot}NAc_2$, is obtained when 2 : 6-dibromoaniline (1 mol.) is boiled for an hour with acetic anhydride (4 mols.). The product is poured into water and after standing for some time, filtered, dried, and crystallised from light petroleum (b. p. 80—90°). It forms well-developed, hard, transparent prisms melting at 100—101° and readily soluble in the usual organic solvents.

0·1789 gave 0·2038 AgBr. Br = 48·47.
0·1735 „ 0·1974 AgBr. Br = 48·41.
$C_{10}H_9O_2NBr_2$ requires Br = 47·8 per cent.

I hope shortly to be able to start experiments in order to determine the relative influence of different ortho-substituents (Me, Cl, Br, I, NO_2, &c.) both on the formation and hydrolysis of mono- and di-acetylarylamines.

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LIX.—*A Form of Tautomerism occurring amongst the Thiocyanates of Electronegative Radicles.*

By Augustus Edward Dixon, M.D.

It is well known that the isomerism subsisting between the normal thiocyanates of fatty or benzenoid hydrocarbon radicles on the one hand, and the *iso*thiocyanates (thiocarbimides) on the other, differs markedly from that which obtains between the corresponding derivatives of certain unsaturated hydrocarbon groups.

In the former case, a thiocarbimide, R·NCS, once produced, continues to act as such under all ordinary chemical treatment; it is

quantitatively desulphurised by silver, or alkaline lead, salts, yields molecular additive compounds with nitrogenous bases, and when treated with ferric salts gives no reaction whatever for thiocyanic acid. In like manner, a thiocyanate, R·SCN, once formed, exhibits great stability, and is for all practical purposes incapable of behaving as, or being converted into, a thiocarbimide.

In the latter case, this does not exactly hold; allyl thiocyanate, for instance, changes gradually on standing, or at once on heating, into the isomeric thiocarbimide, but once accomplished, this change is permanent, in the sense that it cannot by any known means be directly reversed.

The above remarks apply solely to combinations of the ·SCN or ·NCS group with distinctly electropositive radicles; amongst compounds of electronegative organic radicles with the groups in question, marked variations from the characters just indicated are observable, of which the most prominent is a tendency towards a kind of tautomerism. This phenomenon is manifested in respect of the CSN atomic complex, which may act either as ·SCN or ·NCS, or sometimes as both simultaneously, so that, as a rule, it cannot be asserted that a given compound behaves rather as a thiocyanate or a thiocarbimide until the conditions are defined under which it is observed to act.

Accounts have been given in previous communications of a number of such substances and their derivatives; the compounds themselves are prepared by acting with certain metallic thiocyanates upon acid chlorides, usually in presence of a solvent; in the main, and so far as they have been examined, their properties are akin to those of the alkyl thiocarbimides, and consequently they have all appeared under the name of "thiocarbimides" (compare Trans., 1892, **61**, 529; 1895, **67**, 565, 1040; 1896, **69**, 855, 1593; 1897, **71**, 617; 1899, **77**, 385, 388).

In relation to water, however, these substances commonly exhibit the characters of thiocyanates, undergoing hydrolysis more or less readily, with formation of thiocyanic acid:

$$R{\cdot}CO{\cdot}NCS + H_2O = R{\cdot}CO{\cdot}OH + HSCN,$$

and for this reason they cannot be separated from mixtures by the method of distillation in a current of steam, which is generally employed for their congeners of the purely hydrocarbon class.

As a rule, they unite equally readily with ammonia or nitrogenous organic bases, yielding thioureas or thiocarbamides, but it happens not unfrequently that a given compound of this class will behave almost quantitatively as a thiocarbimide towards an organic base, whilst if treated with ammonia, even although the latter be cautiously added and care taken to avoid excess, no thiourea, or practically none,

is formed, but ammonium or other thiocyanate instead; acetyl and stearyl thiocarbimides may be cited as cases in point.

Occasionally this tautomerism, if it may be so called, becomes still more limited, and, ceasing to depend on the varying nature of the bases presented, resolves itself almost entirely into a question of temperature. The author's assistant, Mr. R. E. Doran, has recently observed that, according to the temperature at which the operation is carried out, acetyl thiocarbimide is capable of yielding, with aniline, either acetylphenylthiocarbamide or aniline thiocyanate as main product, and hopes shortly to make a communication on the subject.

Certain non-metallic mineral chlorides are also known to exchange their halogen for the organic residue of lead and other metallic thiocyanates; the products thus obtained decompose readily on contact with water, thereby yielding thiocyanic acid, and consequently have always been regarded as thiocyanates pure and simple. They are: phosphorus thiocyanate, $P(SCN)_3$; arsenic thiocyanate, $As(SCN)_3$; silicon thiocyanate, $Si(SCN)_4$, all prepared by Miquel (*Ann. Chim. Phys.*, 1877, [v], 11, 343, &c.). In addition to these, a substance having the empirical composition of thionyl thiocyanate has been described by McMurtry (Trans., 1889, 55, 48) as resulting from the interaction of thionyl chloride and mercuric thiocyanate; it appears not to be strictly analogous to the preceding, and will be referred to presently.

The essential mode of preparation and the characters of the substances just mentioned (with the exception of McMurtry's compound), so far as they have been recorded, are somewhat similar to those of the acidic organic thiocarbimides; consequently, in view of the "tautomeric" phenomena presented by the latter, it seemed desirable to investigate more closely the action of thiocyanates on the chlorides of some electronegative mineral elements, or groups, in order to learn whether the products might not equally be capable, when placed under suitable conditions, of acting as thiocarbimides. This inquiry had, moreover, a special interest, for hitherto no isomerism (or tautomerism) has been established amongst mineral derivatives analogous to that subsisting between the normal and *iso*thiocyanates of organic radicles.

In attempting to obtain a satisfactory answer to the question here raised, a good deal of experimental difficulty has been encountered; qualitative evidence that isomerism or tautomerism exists may easily be secured but the isolation, in a pure state, of such compounds as are suitable for definitely establishing it is greatly hindered by various causes; for instance, the readiness with which many of them undergo hydrolysis, and the fact that the mineral thiocyanates cannot, as a rule, be distilled, even in a vacuum, without decomposition.

It was the intention of the author to refrain from publishing any

account of the work done in the direction indicated until more decisive results should be forthcoming, but recently the study of acid thiocarbimidic derivatives has begun to engage the attention of a number of chemists, and it therefore seemed best, with a view to avoid collision with the work of others, to give a brief description of the principal results hitherto attained. Notwithstanding that upwards of fifty distinct experiments have now been conducted on the interaction of thiocyanates with the mineral chlorides named below, and with certain others (for instance, chromyl chloride, stannic chloride, and the chlorides of phenylsulphonic and ethylsulphuric acids), it must be admitted that the precise mechanism of the chemical changes is still far from clear, and the present paper is therefore put forward merely as an instalment. As the study is not yet completed, it has been considered unnecessary to give details of the experiments, save those requisite to explain the general line of work, and to support such conclusions as may be drawn provisionally.

Generally speaking, the method of operating was as follows. The chloride, dissolved in a suitable anhydrous solvent, was added to a considerable excess of dry, finely-powdered thiocyanate (the lead, mercury, copper, ammonium, potassium, and silver salts were all tried), and the mixture either heated or allowed to stand for a month or two at the ordinary temperature; the solid residue was then removed by means of the pump. The filtrate, when shaken with water or mixed with dilute spirit, was tested for thiocyanic acid with ferric chloride, and for thiocarbimidic product by ammoniacal silver nitrate, and by boiling with an alkaline solution of lead. In making the experiments, the following, amongst other chlorides, were used: carbonyl chloride, thionyl chloride, sulphuryl chloride, phosphorus trichloride, phosphorus oxychloride, phosphorus pentachloride; as solvents, carbon disulphide, light petroleum, chloroform, benzene, toluene, xylene, cumene, all carefully dried. In time-experiments, a flask with drying tube was employed; where heat was applied, the mixture was boiled under a reflux condenser, or else heated in a sealed tube. Every product, when examined as described above, proved to contain much thiocarbimide; on the other hand, not one was perfectly free from thiocyanic acid, the amount of which was often considerable, although in a few cases only trifling.

To each product an equivalent quantity of organic base was next added, usually pure aniline; if this caused a precipitate, it was filtered off and examined, otherwise the solution was concentrated by evaporation. In every case, such precipitate, or solid product obtained by concentration, was found to answer to the silver and lead tests for a thiocarbamide.

From these qualitative results, one inference, at least, is clear,

namely, that the ·SCN residue of metallic thiocyanates, when transferred under the above conditions to an inorganic electronegative radicle, no longer retains its purely thiocyanic character in the new product. Nevertheless, it is not entirely lost, since, as indicated above, if treated with boiling water, these compounds, or mixtures, give a more or less intense red coloration with ferric chloride.

In order to establish the thiocarbimidic nature of the products obtainable from metallic thiocyanates and electronegative mineral chlorides, or their capacity to act entirely or in part as such, it was obviously desirable to secure more decisive evidence than that attaching solely to the desulphurisation of their solutions by lead and silver salts. One of the most characteristic and general properties of all true thiocarbamides is their power of uniting directly with primary bases to form thiocarbamides, and consequently attention has been mainly directed towards obtaining such additive products.

It is in this connection that the experimental difficulties before mentioned have been especially prominent. For the thiocarbimides, produced in solution as described above, are usually far from pure: sometimes they contain unaltered chloride, occasionally decomposition products; they invariably give, more or less, the reaction for thiocyanate; and they cannot, any more than their organic congeners, be distilled in a current of steam. Consequently, when treated with a base, the solid product is apt to be a mixture, and hitherto no trustworthy method has been found suitable for extracting the thiocarbamide alone. Moreover, in many cases, the thiocarbamide itself is readily hydrolysed, so that until some better method of working is devised, it is necessary either to identify the latter by its products of hydrolysis, or by analytical figures which are only approximate.

Experiments with Phosphorus Trichloride.

This substance, dissolved in dry benzene, was heated with 1½ to 2 equivalents of lead, or ammonium, thiocyanate, until a fragment of copper oxide, moistened with a drop of the solution ceased to give a green flame coloration.* In one case, where potassium thiocyanate was employed, practically no thiocarbimide was obtained; in ten other experiments, the filtrate, when shaken up with water, was intensely acid, gave a strong red coloration with ferric chloride, and was copiously desulphurised by ammoniacal silver nitrate, or by warming with alkaline

* Miquel states (*loc. cit.*, p. 348) that "en diluant le chlorure de phosphore dans l'éther anhydre, ou dans tout autre liquide inerte, il perd la propriété d'attaquer les sulfocyanates métalliques." The present writer's experience is different, for he finds that a quantity of dissolved product, sufficient to give marked desulphurisation with lead and silver salts, can be obtained after two or three minutes' boiling of a solution of phosphorus trichloride in pure ether with dry lead thiocyanate.

lead tartrate. From the two latter results, the presence of thiocarbimidic product is inferred; it is uncertain whether the former (thiocyanic) reaction is due to the hydrolysis of phosphorus thiocyanate, or of the corresponding thiocarbimide:

$$P(NCS)_3 + 3H_2O = H_3PO_3 + 3HSCN.$$

To the filtrate, aniline, dissolved in benzene, was slowly added, sometimes in deficiency, sometimes in slight excess, of the amount required by the equation,

$$P(NCS)_3 + 3C_6H_5\cdot NH_2 = P(NH\cdot CS\cdot NH\cdot C_6H_5)_3,$$

supposing the chloride to have been quantitatively converted into $P(NCS)_3$. No very considerable difference was noticed in the results, which may be approximately described as follows:

Slight heat is developed, and a yellowish-white, amorphous precipitate falls; this is sticky at first, but presently hardens; a further small quantity is deposited as the mixture cools down. The solid dissolves to some extent in chloroform, but the solution, if moisture be excluded, does not crystallise; it is very sparingly soluble in benzene, but very freely so in acetone, and in alcohol, by which it is decomposed; when heated with dilute nitric acid, it is oxidised vigorously, with formation of sulphuric and phosphoric acids.

If boiled with water, it melts and gradually dissolves; the resulting solution is intensely acid, gives more or less the reactions for aniline thiocyanate, and on cooling deposits crystals of phenylthiourea; the mother liquor, after treatment with dilute nitric acid, responds to the ammonium molybdate and magnesia tests for phosphoric acid.

The phenylthiourea appears to be produced by hydrolysis:

$$P(NH\cdot CS\cdot NH\cdot C_6H_5)_3 + 3H_2O = H_3PO_3 + 3CSN_2H_3\cdot C_6H_5;$$

it is also left when the alcoholic solution is allowed to evaporate; moreover, the original solid, even if left exposed to the moist air of the laboratory (but not if kept in a desiccator), very slowly changes to a crystalline mass consisting largely of this substance. That the phosphorus does not exist as a salt of phosphorus anilide, $P(NH\cdot C_6H_5)_3$, may be inferred from the fact that the solid, if freshly ground up with cold water, yields a filtrate containing mere traces of phosphorus; if the residue be washed repeatedly with water, this element is continuously, but slowly, withdrawn, apparently by hydrolysis, as explained above.

There was considerable variation in the melting points observed for the crude products; one specimen melted at 65°, another at 77° another at a somewhat higher temperature, and in no case was the melting point sharp. As might have been expected, the analytical

results from different preparations were very discordant, a number of sulphur determinations yielding from 17·8 to 21·4 per cent., whilst the phosphorus varied from 2·5 to 5·4 per cent. No method hitherto tried for isolating the constituents of these mixtures, either by extraction, crystallisation, or precipitation of a solution, has proved successful.

As the dissolved products obtained from lead thiocyanate and phosphorus trichloride were obviously impure, an attempt was made to get a pure specimen of phosphorus trithiocyanate by distilling the solution (in dry commercial benzene) under reduced pressure. The solvents came over below 50° under 30 mm. pressure, leaving a reddish-yellow, clear, dense oil, which gave the reactions for thiocyanate, thiocarbimide, and phosphorus. When this was further heated under the same pressure, it darkened somewhat up to 105°, when there were signs of boiling, although nothing distilled over. The thermometer now rose quickly to 170°, at which temperature the contents of the flask suddenly changed, without evolution of gas, to a sticky, black solid, which presently became hard and brittle. This was insoluble in water, and only very sparingly soluble in alcohol, but easily so in warm alkali, yielding a dark red solution, which contained little thiocyanate, but was desulphurised by boiling with ammonia and silver nitrate; it was oxidised vigorously by nitric acid, with production of sulphuric and phosphoric acids. Possibly it is a polymeric form of $P(NCS)_3$, analogous to the "metabenzoylthiocarbimide" of Miquel, $[C_6H_5\cdot CO(CNS)]_n$ (*loc. cit.*, p. 304); but the experiment, so far as the isolation of phosphorus thiocyanate is concerned, was a failure.

The evidence for the existence of $P(NCS)_3$, or a compound capable of behaving as such, and of the corresponding $P(NH\cdot CS\cdot NH\cdot C_6H_5)_3$, is therefore so far imperfect that neither compound has actually been obtained in a state of purity. On the other hand, the benzene solution gives abundantly those metallic reactions whereby the presence of a thiocarbimide, or some immediate derivative, is commonly ascertained, and the dissolved constituent unites spontaneously with a primary base, to afford a product out of which, by mere dissolution in water, a typical thiourea originates.

Action of o-Toluidine.—Pure *o*-toluidine, diluted with dry benzene, was added to a cumene solution of "phosphorus trithiocyanate"; the precipitated amorphous solid, after several washings, first with benzene and then with light petroleum, was dried at a gentle heat in a current of dry air; it formed a yellowish, granular powder, beginning to shrink at 79—80°, and melting slowly between 81° and 83°, to a clear brown liquid.

When treated in alcoholic solution with silver, or alkaline lead, salts, it was very easily and copiously desulphurised, its properties in this and all other respects generally resembling those of the corresponding phenylic derivative. As was to be anticipated from the want of sharpness in the melting point, it proved to be somewhat impure, containing a very perceptible amount of toluidine thiocyanate. The latter could not be extracted by water, even in the cold, without decomposing the main product; an attempt to remove it by boiling the powder with dry benzene also failed, the melted residue forming a stiff, glue-like, brown mass which was still impure.

In order to learn whether the original product had approximately the composition required for the formula $P(NH\cdot CS\cdot NH\cdot C_7H_7)_3$, it was analysed with the following results:

Found, N = 16·47; S = 18·31, 18·03; P = 5·67 per cent.

$C_{24}H_{27}N_6S_3P$ requires N = 16·00; S = 18·27; P = 5·89 per cent.

Notwithstanding that the analytical figures obtained differ but little from those calculated, it cannot thence be inferred that the compound is really pure, for not only was toluidine thiocyanate detected in it, but the percentages of the four elements in the latter substance lie rather close to those in the phosphoretted compound, the phosphorus present in this causing but a small increase in the molecular weight as compared with that due to $3CSN_2H_2\cdot C_7H_7$. Nevertheless the conditions under which the parent substance is formed, its thiocarbimidic reactions, its direct union with the base, and the ready conversion by water of the product thus obtained into tolylthiourea and an acid of phosphorus, all point clearly to the existence of a phosphorus compound of this thiourea, although its definite isolation as a chemical individual still remains to be accomplished.

Experiments with Phosphorus Oxychloride.

When a solution of phosphorus oxychloride in dry benzene was boiled with lead thiocyanate, little change occurred. Using toluene as solvent, marked interaction took place, but as this proved to be still incomplete, cumene was substituted with satisfactory results. After a few minutes' boiling, the filtrate no longer contained chlorine, but freely gave the reactions for dissolved thiocarbimide.

To the clear filtrate, aniline, diluted with benzene, was added in equivalent proportion to the oxychloride used, whereupon a yellow solid was deposited. Immediately after precipitation, this tends somewhat to choke the filter, but it granulates on standing, and may then be filtered without difficulty. A specimen thus prepared, well washed

with benzene and dried as far as possible over shredded wax in a vacuum, formed a mobile, pale-yellow powder, whose weight amounted to more than 90 per cent. of that theoretically obtainable from the oxychloride employed, supposing the latter to have been converted, first into phosphoryl trithiocarbimide, and thence into the corresponding phenylated thiourea.

In order to remove the last traces of solvent, the powder was gently warmed in a flask through which dry air was caused to stream for several hours. When heated in a narrow tube, it began to shrink at about 108—109°, and melted at 111—112° to an amber-coloured liquid. Other preparations melted at temperatures approximating to that given; for instance, at about 114—115° and 113—114° in two different experiments, with preliminary softening at two or three degrees below the actual melting point.

Thus obtained, the substance is practically insoluble in cold water. The latter, if poured off from it, is very faintly acid, gives almost no red coloration with ferric chloride, and does not give the reactions for aniline. When boiled with water, however, it gradually dissolves, all save a trace of yellowish, oily matter. The solution is intensely acid, gives a faint reaction for aniline, and a marked one for thiocyanic acid. On cooling and allowing to stand, it deposits phenylthiourea in prisms.

It is insoluble, or nearly so, in ether, chloroform, carbon disulphide, cold benzene, or light petroleum; easily soluble in ethyl acetate, acetone, glacial acetic acid, or nitrobenzene, and very freely so in alcohol. It dissolves also in sulphuric acid and in caustic potash; if hydrochloric acid be added to the latter solution, a precipitate is formed and hydrogen sulphide escapes. The solution in potash is desulphurised with remarkable ease by lead salts; if alkaline lead tartrate be added to it, a white precipitate falls, which gradually changes in the cold through yellow, orange, deep crimson, and brown to full black; the last change occurs at once if the mixture be gently warmed. In like manner, the sulphides of mercury and cadmium are precipitated when these metals, in alkaline solution, are warmed with the solution of the phosphorus compound.

The aqueous solution contains phosphoric acid, as shown by the magnesia and molybdate tests. Since the original solid is nearly insoluble in cold water, and its solution in hot water gives only phenylthiourea on cooling, it would appear that the phosphoric acid is formed by hydrolysis.

Attempts to purify the substance by crystallisation led to no satisfactory result. It does not crystallise from any of the liquids named above as solvents, and though occasionally crystals were deposited, they proved to be only phenylthiourea. Failing any better material,

therefore, a thoroughly washed crude product was analysed, with the following results:

Found, C = 50·15; H = 4·46; N = 16·7; S = 20·07 and 20·62; P = 6·51.

The above figures, save as regards the sulphur, are in fair agreement with those calculated for the formula $C_{21}H_{21}ON_6S_3P$, namely,

C = 50·35; H = 4·26; N = 16·38; S = 19·21; P = 6·20 per cent.

Accordingly, the production of this compound may be represented as follows:

(1) $2POCl_3 + 3Pb(SCN)_2 = 3PbCl_2 + 2PO(NCS)_3$.
(2) $PO(NCS)_3 + 3C_6H_5 \cdot NH_2 = PO(NH \cdot CS \cdot NH \cdot C_6H_5)_3$;

and its decomposition by water into phenylthiourea,

$$PO(NH \cdot CS \cdot NH \cdot C_6H_5)_3 + 3H_2O = H_3PO_4 + CSN_2H_3 \cdot C_6H_5.$$

The last equation does not, however, furnish a complete account of the interaction with water, inasmuch as thiocyanic acid is also produced; it cannot at present be stated whether this originates through some decomposition of the phosphoryl trithiocarbamide, or from the presence of some other material in the crude substance. At all events, the hydrolysis formulated above does not occur quantitatively, for a rough experiment, made by boiling a known weight of material with water, and collecting the phenylthiourea thereby produced, afforded but 33 per cent. of the amount calculated from the equation, and the latter is only given provisionally, until further experiments shall have been carried out.

o-*Toluidine* gave a tenacious paste, dissolving somewhat in the hot mixture of cumene and benzene; it separated on cooling as a clear, brownish oil, which presently hardened to a resin-like substance. The product was very easily soluble in spirit or acetone, the solutions being readily desulphurised by lead, silver, or cadmium salts. The finely powdered solid, if shaken up with cold water, gave up to it a mere trace of thiocyanic acid, but if boiled with water, it mostly dissolved, and the solution now gave a distinct, although not strong, red coloration with ferric chloride; toludine was not detected in the aqueous solution, which, as usual, was intensely acid.

As in the preceding case, all attempts to purify the product of the interaction were abortive; a sample, treated as there described, was partially analysed, with the following results:

Found, N = 14·2; S = 16·3; P = 5·3.
$C_{24}H_{27}ON_6S_3P$ required N = 15·5; S = 17·7; P = 5·7 per cent.

Action of Ammonia.—According to Miquel (*loc. cit.*, p. 351), phosphorus trithiocyanate is decomposed by aqueous ammonia in the same

way as by water, alkalis, and acids, that is, into phosphorous and thiocyanic acids. In order to avoid the hydrolysing action of water, dry ammonia gas was led into a benzene-cumene solution of the corresponding phosphoryl derivative, whereupon a pale yellow, granular solid was precipitated. This, when washed with benzene followed by light petroleum, and dried in a desiccator, melted imperfectly below 60°. The substance was somewhat deliquescent on exposure to ordinary air, dissolved almost completely in water, yielding an intensely acid solution which contained a good deal of ammonium thiocyanate, but was also very freely desulphurised by warming with alkaline solutions of mercury, silver, lead, or cadmium. Phosphoric acid was present, as shown by the molybdic reaction, but apparently *not ready formed*, for when a freshly-made solution in cold water was divided into two parts and one of these treated with excess of ammonia, followed by magnesia mixture, it remained practically clear for a considerable time, whilst the other, if boiled for a few minutes, cooled, and then treated as described, gave an abundant precipitate consisting of ammonium magnesium phosphate. It seems probable, therefore, that the phosphorus exists mainly as $PO(NH{\cdot}CS{\cdot}NH_2)_3$ (representing the thiourea residue as symmetrical), which affords the reaction for phosphoric acid only after hydrolysis. Attempts to remove the ammonium thiocyanate were unsuccessful, the phosphoretted compound dissolving easily in all the solvents of the former, and being readily decomposed. Incidentally, it became necessary to ascertain the solubility relations of ammonium thiocyanate, which, strange to say, do not appear to have been recorded, and may therefore here be mentioned. It is freely soluble in hot methyl or ethyl alcohol, acetone, ethyl acetate, or glacial acetic acid, and moderately so in boiling amyl alcohol and in nitrobenzene, but practically insoluble in chloroform, pure ether, carbon disulphide, benzene, toluene, or light petroleum.

Thionyl Thiocyanate.

In McMurtry's experiment, referred to above, thionyl chloride dissolved in carbon disulphide is allowed to stand for a few days in contact with excess of lead thiocyanate; the solution is then poured off, evaporated in a vacuum, and the residue washed, first with hot benzene and afterwards with ether. The product forms an amorphous, orange powder having the empirical composition of thionyl thiocyanate, $SO(SCN)_2$, nearly insoluble in most solvents, only slightly soluble in ammonia, and not affected by boiling with hydrochloric acid. Similar results are obtained with lead or silver thiocyanate.

This preparation has now been repeated under various conditions, using the thiocyanate of lead, mercury, or potassium; and as solvents, toluene, chloroform, benzene, or light petroleum. The tem-

perature has been varied from the boiling point of toluene (which causes decomposition and evolution of sulphur dioxide) down to that of the laboratory. At the latter temperature, the duration of the experiment has been extended to three months; also, a benzene mixture with potassium thiocyanate has been heated for two hours at 100° in a sealed tube. In no case was the chlorine completely eliminated as metallic chloride; on the other hand, the filtered liquid in every case gave abundantly the reaction for dissolved thiocarbimide. The amorphous, orange product, if thoroughly washed with water, dissolves more or less completely in warm dilute caustic alkali. The solution thus obtained, if acidified with hydrochloric acid and treated with ferric chloride, yields no red coloration or else only a very trifling one, hence it would seem that the compound is not a true thiocyanate. But the solution in alkali, if mixed with solution of lead or mercury and warmed, or if treated with ammoniacal silver nitrate, is copiously blackened, the material thus exhibiting the characteristics of a thiocarbimide. Probably, considering its stability (to which McMurtry calls attention), its indifference to ammonia and its physical state, it will prove to be a polymeric form $[SO(NCS)_2]_n$.

If the clear solution in chloroform, benzene, or light petroleum obtained by digesting thionyl chloride in one of these solvents with a metallic thiocyanate be treated with aniline, a precipitate falls at once, consisting partly of aniline hydrochloride. If this precipitate be filtered off, well washed, and then digested with water in order to remove the aniline salt, a brownish-yellow residue is left, nearly insoluble in boiling alcohol. This substance, when dissolved in alkali, responds freely to the desulphurisation tests for a thiocarbamide.

From these results, it would appear that thionyl chloride, under the conditions stated, is converted, at least in part, into thionylthiocarbimide, $SO(NCS)_2$, or else a polymeride, or probably both; but hitherto the products have been obtained in very limited quantity, and it is yet uncertain whether one or more forms are present. In a three months' experiment at atmospheric temperature, not more than about one-tenth of the chloride used had undergone conversion, and the experiments are being continued, allowing a longer period for interaction, and otherwise varying the conditions.

Carbonyl chloride, dissolved in toluene, gave, with lead thiocyanate, somewhat similar results. On treatment of the product with aniline, carbanilide was formed, together with small quantities of a thiocarbamide melting at about 174°, which has not yet been obtained in a pure state.

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LX.—*Halogen-substituted Thiosinamines.*

By Augustus Edward Dixon, M.D.

In a communication made to this Society in 1892 (Trans., 61, 545), describing the production and properties of $\beta\gamma$-dibromopropylthiocarbimide, the author noted a characteristic wherein it differs from non-halogenised compounds of the same class; namely, that when treated with aniline it affords, not the corresponding dibromopropylphenylthiocarbamide, $CH_2Br\cdot CHBr\cdot CH_2\cdot NH\cdot CS\cdot NH\cdot C_6H_5$, but a basic ring compound, $C_3H_5\cdot Br\langle^{S-}_{N}\rangle C\cdot NH\cdot C_6H_5$, by elimination of the elements of hydrogen bromide.

In a subsequent paper (Trans., 1896, 69, 17), it was established that interaction occurs similarly with ammonia, and with other primary and secondary organic bases; and further, that by union with fatty alcohols, closed chain compounds result in like manner, for instance, $C_3H_5\cdot Br\langle^{S-}_{N}\rangle C\cdot OEt$. Moreover, it was shown (*loc. cit.*) that ready-formed allylthiourea, when treated with bromine or iodine, undergoes precisely the same change, losing hydrogen, so as to yield a compound which is no longer a true thiourea. Disubstituted, and no doubt trisubstituted (*ibid.*, 852), thiosinamines equally fail to add on halogen so as to form a saturated derivative of the parent type.

What is true of the above halogenised alkylic, holds equally for the halogenised fatty acidic thiocarbimides. These also (Trans., 1897, 71, 617) unite spontaneously with primary and secondary bases, but the products are not halogen-substituted acidic thioureas; in every case, a molecule of haloid acid is eliminated, with production of a ring compound—one of the so-called "thiohydantoins," for example:

$$\begin{matrix}CH_2Cl\\ |\\ CO\cdot NCS\end{matrix} + MePhNH = \begin{matrix}CH_2\cdot S\\ |\\ CO-N\end{matrix}\rangle C\cdot NMePh + HCl.$$

By acting upon thiocarbimides with chlorinated and brominated organic bases, Gabriel and his pupils have arrived at similar results; for instance, methylthiocarbimide affords with bromoethylamine (*Ber.*, 1889, 22, 1148), not methylbromoethylthiocarbamide,

$$CH_3\cdot NH\cdot CS\cdot NH\cdot C_2H_4Br,$$

but the hydrobromide of "*n*-methylethylene-ψ-thiourea,"

$$\begin{matrix}CH_2-S\\ |\\ CH_2\cdot N\end{matrix}\rangle C\cdot NH\cdot CH_3.$$

In short, excluding certain nuclear benzenoid compounds, in which the halogen element is retained with exceptional tenacity against

ordinary chemical exchange, it might appear tolerably safe to lay it down as a general principle that halogen-substitution derivatives of the thioureas and thiocarbamides are not obtainable, at least under usual working conditions, either from base and halogenised thiocarbimide, or, conversely, from thiocarbimide and halogenised organic base.

This 'principle' goes on the assumption that substituted allylic groups would be found to interact like their fatty congeners,* and formed the basis of a conjecture made by the author in the second paper cited above (p. 25): "The question arises, therefore, whether . . . the 'chlorallylthiourea' and 'bromallylthiourea,' briefly recorded by Henry (*Ber.*, 1872, **5**, 188) as resulting from the action of ammonia on α-chlor- and brom-allylthiocarbimides respectively, are not also haloid salts, namely, the hydrochloride and hydrobromide of a basic ring compound, $CH_2{:}C\!\!<\!\!\begin{matrix}S\\ CH_2{\cdot}N\end{matrix}\!\!>\!\!C{\cdot}NH_2$."

In order to test the correctness or otherwise of this conjecture, Henry's work on the former has now been re-examined and somewhat extended, with the results detailed below.

β-Chloroallylthiocarbimide, $CH_2{:}CCl{\cdot}CH_2{\cdot}NCS$, *and its Derivatives.*

The best yields were obtained by mixing α-epidichlorohydrin with excess of warm alcoholic potassium thiocyanate, allowing the mixture to stand for some days, shaking occasionally, boiling then for a short time, and distilling in a current of steam; the product, when fractionated, amounted in various experiments to from 50—63 per cent. of the theoretical, and formed a limpid, colourless, highly-refractive oil, boiling at about 182° (corr.), and giving the usual reactions of a thiocarbimide. It is easily soluble in spirit and slightly so in water, smells pungently of oil of mustard, and readily blisters the skin.

Action of Ammonia.—Interaction occurred spontaneously, with marked development of heat, on the addition of alcoholic ammonia, and a white, crystalline solid was presently deposited containing no trace of ammonium chloride. When recrystallised from benzene mixed with a little spirit, and then from benzene alone, the substance was obtained in slender, vitreous prisms, which dissolve moderately easily in cold water, sparingly in cold benzene, very freely in alcohol, and melt sharply at 93·5—94·5° (corr.); Henry gives 90—91°.

* So far as desulphurisation of the thioureas by means of alkaline lead solution is concerned, it has already been shown (Trans., 1893, **63**, 319) that the unsaturated (allyl) group plays a part closely resembling that of the saturated hydrocarbon radicles.

The aqueous solution is perfectly neutral to litmus, that in alcohol, when mixed with silver nitrate, yields no precipitate, but the mixture blackens instantly on the addition of ammonia; moreover, the aqueous solution, when treated with silver nitrate, affords a white silver compound which dissolves in concentrated nitric acid; the solution thus obtained gradually becomes turbid on standing, or if heated undergoes vigorous oxidation, and silver chloride at once separates. The compound also dissolves in cold sulphuric acid; if this solution be diluted and mixed with silver nitrate, it remains clear, but if heated it decomposes, with evolution of sulphur dioxide and hydrogen chloride.

From these results, the inference is plain; silver fails to withdraw the combined halogen element directly, save on complete disruption of the molecule, and therefore, contrary to anticipation, the compound is not a hydrochloride, but presumably a true thiourea. Any doubt on the latter head was removed by the result obtained on treatment with alkaline lead tartrate, which gave a clear solution, blackened copiously on warming, with formation of lead sulphide; this reaction, common to all monosubstituted thioureas, does not occur with the basic ring compounds usually obtained from halogenised fatty bases or thiocarbimides. Henry's description of the preparation and properties of his compound (*loc. cit.*, and *Compt. rend.*, 1882, **95**, 850) occupies but a few lines; it appears to have been only incidentally produced, and it is scarcely likely that he concerned himself to ascertain whether or not it really was a thiourea, no reason then existing to suspect that it might be something else. However this may be, the formula assigned by him requires no modification, save that the compound, like other monosubstituted thioureas, is probably not of the symmetrical type, but a derivative of imidothiocarbamic acid, either

$CH_2{:}CCl{\cdot}CH_2{\cdot}N{:}C(SH){\cdot}NH_2$ or $NH{:}C(SH){\cdot}NH{\cdot}CH_2{\cdot}CCl{:}CH_2$.

The $\beta\gamma$-dibromopropylurea obtained by Andreasch (*Monats.*, 1884, **5**, 38), from allylurea and bromine, or from $\beta\gamma$-dibromopropylamine hydrochloride and potassium cyanate (Paal and Heupel, *Ber.*, 1891, **24**, 3038), is stated by the former to be converted by boiling with water into the hydrobromide of "bromopropylene urea," $CO\langle^{NH}_{NH}\rangle C_3H_5Br$. In order to ascertain whether molecular rearrangement would occur with β-chloroallylthiourea under like conditions, its dilute aqueous solution was boiled down to a small bulk; the crystals which separated on cooling were, however, nothing but unchanged chloroallylthiourea, and the mother liquor, which still remained neutral, proved to contain not a trace of combined hydrochloric acid.

Chloroallylthiohydantoin.—Chloroallylthiourea was melted on the water-bath with something more than 1 molecular proportion of monochloroacetic acid. Presently a brisk reaction set in, with evolution of hydrogen chloride; the residual oil, while still warm, was mixed with alcohol, and thereupon solidified to a white, crystalline mass, consisting of the hydrochloride of chloroallylthiohydantoin. The product, after several washings with alcohol, in which it is very sparingly soluble, turned slightly brown at 170°, and melted, with blackening, at 185—186° (corr.).

Found, HCl = 16·5. $C_6H_7ON_2ClS,HCl$ requires HCl = 16·1 per cent.

The interaction occurs as follows:

$$CSN_2H_3\cdot C_3H_4Cl + CH_2Cl\cdot CO_2H = C_3H_4Cl\cdot N{:}C\begin{matrix}S\text{—}CH_2\\ NH\cdot CO\end{matrix},HCl.$$

On recrystallising a portion of the hydrochloride from water, the combined acid was withdrawn and neutral prisms were deposited; they melted at 149°, and consisted of the free thiohydantoin.

The main portion was dissolved in tepid water, in which it is moderately easily soluble, and the solution exactly neutralised by caustic alkali; the crystalline precipitate thus obtained gave the following result on analysis:

Found, S = 16·9. $C_6H_7ON_2ClS$ requires S = 16·82 per cent.

β-Chloroallylthiohydantoin, or [using the nomenclature proposed by the writer (Trans., 1897, 71, 637)] *n*-β-chloroallylthiourantoin, is moderately soluble in hot water, sparingly so in cold water or in benzene, easily so in hot alcohol or in cold dilute alkali; the solution in alkali is not desulphurised by boiling with alkaline lead tartrate. From water it crystallises in pearly leaflets, resembling thiocarbanilide in appearance; from spirit, in brilliant, vitreous prisms; both forms melt at the same temperature, namely, 149° (corr.).

The solution in spirit gives no precipitate with neutral silver nitrate; with the ammoniacal nitrate, a white silver compound is produced, soluble in excess of ammonia or in nitric acid; if the latter solution be boiled, vigorous oxidation occurs, with formation of silver chloride.

When boiled for a short time with dilute caustic alkali, the substance is decomposed, with production of thioglycollic acid; if the escaping gases are led into water, mere traces of ammonia and chlorine are found; the change, therefore, appears to occur mainly as follows:

$$C_3H_4Cl\cdot N{:}C\begin{matrix}S\text{—}CH_2\\ NH\cdot CO\end{matrix} + 2H_2O =$$
$$C_3H_4Cl\cdot NH\cdot Cl\cdot NH_2 + SH\cdot CH_2\cdot CO_2H,$$

the former product undergoing hydrolysis to some extent, yields carbon dioxide, ammonia, and chloroallylamine.

When boiled for an hour with dilute hydrochloric acid, the substance yielded a brownish oil; this was insoluble in cold dilute alkali, but dissolved on boiling, with evolution of ammonia and formation of thioglycollic acid; it is therefore probably chloroallylthiocarbimidoglycolide, $C_3H_4Cl\cdot N{:}C\begin{matrix}S\cdot CH\\ |\\ O\cdot CO\end{matrix}$ (Trans., 1897, **71**, 623), but the amount obtained was not sufficient to admit of purification for analysis.

Action of Aniline.—Slight heat was developed on mixing aniline and chloroallylthiocarbimide in alcoholic solution, and presently a yellowish solid was deposited, the yield being practically quantitative; when twice recrystallised from benzene, using animal charcoal, it was obtained in pearly, six-sided plates melting at 91—92° (corr.). The formula was checked by a sulphur determination.

Found, S = 14·1. $C_{10}H_{11}N_2ClS$ requires S = 14·14 per cent.

The compound is rather sparingly soluble in boiling water (from which it crystallises in long, thin needles) and in hot light petroleum, but dissolves freely in alcohol. It dissolves in warm alkali (from which it separates on cooling, or on neutralisation by hydrochloric acid) and in warm, concentrated hydrochloric or sulphuric acid. The latter solutions are reprecipitated on cautious addition of water, but a large excess of water again dissolves the precipitate; the solution in sulphuric acid is decomposed by heating, with production of a pinkish colour and liberation of fumes of hydrogen chloride.

Like its congener, already described, this compound is non-saline in character; it is perfectly neutral to litmus; its cold alcoholic solution is not precipitated by silver nitrate, but the mixture slowly darkens (if ammonia be added, it blackens at once), and it is freely desulphurised by heating with alkaline lead tartrate. Its formation is represented as follows:

$$CH_2{:}CCl\cdot CH_2\cdot NCS + NH_2\cdot C_6H_5 = C_6H_5\cdot NH\cdot CS\cdot NH\cdot CH_2\cdot CCl{:}CH_2,$$

the product being, accordingly, *ab*-*β*-chloroallylphenylthiocarbamide.

An experiment was made in order to learn whether molecular rearrangement into the ring form, $CH_2{:}\begin{matrix}C\text{——}S\\ |\\ CH\cdot N\end{matrix}\!\!>C\cdot NH\cdot C_6H_5,HCl$, would be effected by heat. A quantity of the pure thiocarbamide was slowly brought to a temperature of 30° above the fusing point, and there maintained for a short time; on further raising the temperature, signs of decomposition commenced, with marked darkening, and evolution of the odour of mustard-oil, whereupon the heating was stopped, and the fused mass allowed to solidify. On heating again, the melting

point, instead of having risen, as was to be expected if a hydrochloride had been formed, proved to be a couple of degrees lower than at first; and the product, when recrystallised, was found to be in all respects identical with the material taken for experiment.

Another quantity was boiled down with water, as described for β-chloroallylthiourea, but this also failed to bring about any change.

When treated in hot alcoholic solution with a trifle over the calculated quantity of silver nitrate, the corresponding *β-chloroallylphenylcarbamide* was obtained in slender prisms melting at 151—152° (corr.). It is moderately easily soluble in alcohol, and rather sparingly so in boiling water, yielding a neutral solution, which is not precipitated either by ordinary or ammoniacal silver nitrate. Analytical results:

Found, N = 13·5; Cl = 16·43.

$C_{10}H_{11}ON_2Cl$ requires N = 13·34; Cl = 16·84 per cent.

Action of o-*Toluidine.*—An oil was obtained which solidified after a few days' standing in a vacuum over sulphuric acid; when recrystallised from a mixture of benzene and light petroleum, and then from weak spirit, it occurred in vitreous prisms melting at 84—85°. The yield amounted to 77 per cent. of the theoretical.

Found, S = 13·2. $C_{11}H_{13}N_2ClS$ requires S = 13·32 per cent.

Chloroallyl-*o*-tolylthiocarbamide is practically insoluble in cold water or light petroleum, but easily soluble in benzene, and very freely so in alcohol; its solution in the last-named solvent behaves with lead and silver salts like the phenylic homologue.

Action of p-*Toluidine.*—The product occurred in colourless, triclinic plates nearly insoluble in water, moderately soluble in boiling alcohol, and melting at 127—128° (corr.). Its properties are similar to those of the phenyl homologue.

Found, N = 11·77; S = 13·3.

$C_{11}H_{13}N_2ClS$ requires N = 11·67; S = 13·32 per cent.

Action of Benzylaniline.—The substance was prepared and purified as described for the *o*-tolyl compound; after a final crystallisation from light petroleum, it was obtained in fine, silvery needles melting at 77—78°. It is practically insoluble in water or alkali, and somewhat sparingly soluble in light petroleum, but dissolves easily in hot, moderately in cold, spirit, and very freely in benzene or chloroform. The alcoholic solution gives no precipitate with silver nitrate, but the mixture blackens on warming; with the ammoniacal nitrate, a white, curdy precipitate falls, which dissolves on heating without blackening. The substance is not desulphurised by boiling with alkaline tartrate of lead.

Found, S = 10·1. $C_{17}H_{17}N_2ClS$ requires S = 10·12 per cent.

Action of Piperidine.—Interaction occurred at once on mixing alcoholic solutions of the constituents, the mixture quickly setting to a white, crystalline magma; the yield was quantitative. By recrystallisation from boiling alcohol, the substance was obtained in beautiful, transparent, quadrangular plates of remarkable brilliancy; they melted, apparently without decomposition, between 146·5° and 147·5 (corr.). Analytical results: *

Found, Cl = 16·3; N = 13·2; S = 14·86.

$C_9H_{15}N_2ClS$ requires Cl = 16·20; N = 12·85; S = 14·66 per cent.

The compound is insoluble in water, but moderately soluble in hot alcohol; its solution is not affected by boiling with alkaline lead tartrate. Silver nitrate causes no precipitate in the cold, but the mixture blackens on boiling; with the ammoniacal nitrate, a white silver compound is precipitated; on heating, this decomposes, yielding silver sulphide. Like the preceding compounds, therefore, this is not a hydrochloride, but chloroallylpiperidylthiourea, probably $CH_2{:}CCl{\cdot}CH_2{\cdot}N{:}C(SH){\cdot}C_5NH_{10}$.

Action of Benzylamine.—The constituents were mixed in alcoholic solution, and the solvent allowed to evaporate gradually; a sticky, brown solid was left, which was purified by repeated recrystallisation from a mixture of two volumes of light petroleum with one of benzene. The product eventually separated in rosettes of flat prisms having a very brilliant, pearly lustre and melting at 69°.

Found, N = 11·7. $C_{11}H_{13}N_2ClS$ requires N = 11·67 per cent.

The substance is nearly insoluble in boiling water and in light petroleum; very freely soluble in methyl or ethyl alcohol, ether, chloroform, acetone, benzene, or carbon disulphide. Silver nitrate added to the alcoholic solution causes no precipitate, but the mixture darkens slowly on standing, or at once blackens on the addition of ammonia; if treated with nitric acid, it is violently oxidised, and silver chloride separates. Like other disubstituted thiocarbamides whose substituting groups are non-benzenoid in character, chloroallylbenzylthiocarbamide is not desulphurised by ordinary treatment with alkaline tartrate of lead.

Action of Phenylhydrazine.—Heat was evolved on mixing the con-

* Some difficulty was experienced in determining the percentage of sulphur in this as well as in the preceding compound. By the method commonly used in this laboratory—namely, evaporation with aqueous or weak alcoholic sodium hydroxide, and fusion of the dry product with nitre—figures were obtained varying from 8·3 to 13·5 per cent. Preliminary attack with fuming nitric acid, followed by treatment as above, gave equally discordant results, three determinations affording 6·8, 7·9, and 12·9 per cent. respectively; the method eventually adopted was fusion with dry sodium carbonate and nitre.

stituents in alcoholic solution; this was checked by external cooling with water, and presently crystalline matter separated. When several times recrystallised from somewhat diluted alcohol, the product formed white prisms melting at 107—108° (corr.).

Found, S = 13·34. $C_{10}H_{12}N_3ClS$ requires S = 13·26 per cent.

α-Chloroallyl-β-phenylthiosemicarbazide,

$$C_3H_4Cl\cdot NH\cdot CS\cdot NH\cdot NH\cdot C_6H_5,$$

is practically insoluble in water, easily soluble in alcohol; its solution is not desulphurised by boiling with alkaline lead tartrate. It gives no precipitate with neutral or ammoniacal nitrate of silver (and hence, although containing chlorine, is not a hydrochloride), but the latter mixture is blackenend by heating. The solution in weak alcohol, if mixed with excess of caustic alkali, followed by a few drops of copper sulphate, gives a black precipitate; if this be warmed, it changes to red, becoming reduced to cuprous oxide.

β-Chloro-$\beta\gamma$-dibromopropylthiocarbimide, $CH_2Br\cdot CClBr\cdot CH_2\cdot NCS$, *and its Derivatives.*

To β-chloroallylthiocarbimide (1 mol.), dissolved in about five times its own volume of chloroform, and cooled by means of a freezing mixture to $-10°$, bromine (1 mol.), also dissolved in chloroform, was slowly added. Combination occurred less readily between these constituents than when allylthiocarbimide is similarly treated; the bromine, as judged by the colour of the mixture, showed at first no sign of being absorbed, but in the course of about half an hour the solution had lost its deep-red colour (becoming pale-yellow) and its pungent smell. A not inconsiderable quantity of a yellowish-red, treacly deposit was found sticking to the bottom of the vessel, resembling in appearance and consistency a product which is always obtained in small quantity during the preparation of dibromopropylthiocarbimide; the clear solution was decanted from this, and the chloroform distilled off on the water-bath. The residue was now distilled in a current of steam; a little chloroform first came over, and then the mustard oil; the latter distils rapidly, although less so than chloroallylthiocarbimide. It formed a dense liquid of pale reddish-yellow colour and faintly pungent odour, giving the usual thiocarbimidic reactions with lead and silver salts. Like the corresponding $\beta\gamma$-dibromopropylthiocarbimide, it is not very freely soluble in 90 per cent. alcohol. Analysis was considered unnecessary, in view of the well-marked compounds which it gave with aniline and benzylamine.

Action of Aniline.—Alcoholic solutions were mixed, and presently a good crop of a yellow, crystalline solid was deposited; when recrys-

tallised from weak spirit, it formed a sandy powder, melting at 112—113° (corr.).

On analysis, figures were obtained agreeing with those required for an additive compound:

Found, S = 8·5 and 8·25; Cl + Br = 50·9.

$C_{10}H_{11}N_2ClBrS$ requires S = 8·29; Cl + Br = 50·54 per cent.

The substance is almost insoluble in concentrated hydrochloric acid, very sparingly soluble in water or light petroleum, moderately easily so in alcohol, and freely in chloroform, acetone, benzene, or carbon disulphide. It is insoluble in cold dilute potash, but the mixture is decomposed on warming, with formation of potassium bromide, &c.

The solution in weak spirit is faintly acid to litmus; it gives with nitrate of silver a whitish precipitate; if this be mixed with a slight excess of ammonia, the resultant silver sulphide filtered off, and the filtrate acidified by nitric acid, no precipitate is formed. Consequently, the compound is not a hydrochloride. But weak alkali, added to the cold dilute alcoholic solution, withdraws bromine; therefore it is a hydrobromide.

With the view of obtaining the corresponding base, the hydrobromide, in weak spirit, was mixed with a trifle over the calculated quantity of normal soda, and the resultant solution allowed to evaporate at the ordinary temperature; the product was then washed repeatedly with water until the washings ceased to give the reaction for sodium bromide; but a dirty brown paste was left, which could not be got into a fit state for analysis. The experiment was carefully repeated, but led to no satisfactory result.

An attempt was next made to combine bromine with chloroallylphenylthiocarbamide, in the hope of thus obtaining the above chlorodibromo-derivative. The bromine, dissolved in chloroform, was very slowly added to a cooled alcoholic solution of the thiocarbamide; it was instantly absorbed, but the mixture quickly became turbid, owing to the deposition of free sulphur, and on evaporation of the filtered liquid a dirty brownish-red, treacle-like mass was formed which did not appear to contain the desired product; the phenomena, in fact, were much the same as those observed in a case where bromine and allylphenylthiocarbamide were caused to interact with the view of obtaining an additive compound (Trans., 1896, **69**, 852).

The chlorodibromo-derivative is very slightly desulphurised by boiling with alkaline lead solution, the darkening observed being most likely due to the presence of a trace of chloroallylphenylthiocarbamide, but it consists, substantially at all events, of the hydro-

bromide of a ring compound, either $CClBr<\begin{matrix}CH_2\cdot S\\CH_2\cdot N\end{matrix}>C\cdot NHPh$, or $CH_2Br\cdot CCl<\begin{matrix}S\\CH_2\cdot N\end{matrix}>C\cdot NHPh$, or one of the (imidic) tautomeric forms.

The attempts to isolate a pure basic product from the phenylic salt having failed, an experiment was next tried using a fatty amine.

Action of Benzylamine.—Before mixing, the materials were freely diluted with alcohol; the mixture at once became warm, and the odour of both constituents was quickly lost. After allowing the solvent to evaporate slowly at the ordinary temperature, an acid oil was left, which became tenacious on keeping over sulphuric acid in a vacuum, but showed no sign of crystallisation at the end of a week. It was then dissolved in weak spirit, and the solution treated with a molecular proportion of normal alkali; a brownish, crystalline substance was thereby precipitated, the mother liquor from which proved to contain much alkali bromide. The precipitate was twice recrystallised from weak alcohol, using animal charcoal; it separated in rosettes of pointed prisms, still retaining a brownish tinge, which was eventually got rid of by recrystallisation from light petroleum. Thus purified, it formed long, flattened prisms, having a very brilliant, pearly lustre, and melting at 107—108° (corr.). If cautiously heated over a small gas-flame, the substance first melts to a water-clear liquid; at a higher temperature, this suddenly acquires an intense purple colour, resembling that of potassium permanganate; in another moment it decomposes almost explosively, evolving hydrogen sulphide, and leaving a carbonised, deep brown residue.

On analysis, figures were obtained agreeing fairly with those required for the free penthiazoline base, $BrClC<\begin{matrix}CH_2-S\\CH_2\cdot N\end{matrix}>C\cdot NH\cdot C_7H_7$, or its isomeride, $CH_2Br\cdot CCl<\begin{matrix}S\\CH_2\cdot N\end{matrix}>C\cdot NH\cdot C_7H_7$.

Found, S = 10·34; N = 8·98; Cl + Br = 36·99.

$C_{11}H_{12}N_2ClBrS$ requires S = 10·03; N = 8·79; Cl + Br = 36·11 per cent.

The substance melts when heated with water, in which, however, it is nearly insoluble; it is somewhat sparingly soluble in boiling light petroleum, but very freely soluble in ether or hot alcohol; it dissolves also in warm dilute hydrochloric or hydrobromic acid, the former solution giving no reaction for bromine when treated with chlorine water; the latter, when evaporated down, leaves the hydrobromide as a tenacious oil. The alcoholic solution affords with silver nitrate a whitish precipitate, scarcely affected by ammonia in the cold, but darkening gradually when boiled with it. Alkaline lead tartrate produces a white precipitate, which dissolves on heat-

ing; the solution, when boiled, does not remain perfectly clear, but undergoes a trifling desulphurisation; the base, therefore, was probably not quite pure, although its melting point, after three recrystallisations, varied by only 1°.

Summary.

The results of the above experiments may be summarised as follows: (1) β-Chloroallylthiocarbimide unites directly with ammonia, and with primary and secondary bases, thereby yielding the corresponding substituted chlorinated thioureas or thiocarbamides; these substances possess properties similar to those of their non-chlorinated allies. (2) β-Chloroallylthiocarbimide absorbs bromine to form β-chloro-βγ-dibromopropylthiocarbimide; this substance also unites with organic bases, but with elimination of half the bromine as hydrogen bromide, and formation of saline ring compounds, analogous to those obtained from other halogenised fatty bases and thiocarbimides, or from halogenised fatty thiocarbimides and nitrogenous bases.

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LXI.—*Researches on Morphine. Part II.*

By S. B. SCHRYVER and FREDERIC H. LEES.

IN our last communication (Trans., 1900, 77, 1024), we showed that when morphine, $C_{17}H_{19}O_3N$, is treated with phosphorus tribromide, the alcoholic hydroxyl group is replaced by a bromine atom, and bromomorphide, $C_{17}H_{18}O_2NBr$, is obtained. This substance, on treatment with water, decomposes according to the equation:

$$C_{17}H_{18}O_2NBr + H_2O = C_{17}H_{19}O_3N,HBr.$$

The base, isomeric with morphine, obtained from this hydrobromide was designated *iso*morphine. Further investigation, however, has revealed the fact that the product is a mixture of the hydrobromides of *two* isomeric bases, neither of which is identical with morphine. The properties of *iso*morphine, as given in our last paper, are correctly described, since, by the methods of purification adopted, it was obtained quite free from the second isomeride, for which we now propose the name β-iso*morphine*. The latter substance is obtained in much smaller quantities than *iso*morphine; its specific rotation is considerably higher, and it is characterised by the fact that it crystallises with ½-mol. of

alcohol, which is only expelled after prolonged heating at 120°, as well as by the fact that the free base is readily soluble in cold water. The method of separation of *iso*morphine from *β-iso*morphine is described in detail in the experimental part of this paper, and the further investigation of these bases is reserved by one of us (F. H. L.).

It was pointed out in our previous communication that *iso*morphine differs markedly from morphine in its physiological behaviour, and in view of this fact it appeared of interest to determine as fully as possible the chemical relationship between these two isomerides. For this purpose, a long series of investigations was instituted.

On treatment with acetic anhydride, *iso*morphine yields a *diacetyl* derivative, $C_{17}H_{17}ON(O{\cdot}CO{\cdot}CH_3)_2$, which was isolated in the form of a crystalline methiodide.

Phosphorus tribromide, as also hydrobromic acid, reacts with *iso*morphine and regenerates bromomorphide. This reaction with phosphorus tribromide is in marked contrast to that with phosphorus trichloride. Although *iso*morphine was treated with the latter reagent several times, and under varying conditions, in no case could any chloromorphide be obtained. The only product that could be isolated was a syrupy base, which readily oxidised on exposure to air. It was pointed out in the previous paper that chloromorphide is strongly lævorotatory. The investigation of the action of water on chloromorphide, which is described in detail below, has revealed the fact that different products are obtained from chloromorphide and bromomorphide, and we have reason to believe that the two substances are not chemically analogous, that is, they are not respectively the chloro- and bromo-derivatives of the same base. Bromomorphide is possibly bromo*iso*morphide, since both morphine and *iso*morphine, on treatment with phosphorus tribromide, yield the same bromo-derivative.

Further experiments described in this paper relate to the exhaustive methylation of *iso*morphine. It was shown in our last paper (*loc. cit.*, p. 1039) that *iso*morphine methiodide, on treatment successively with molecular quantities of silver sulphate and barium hydroxide, yields a product to which a phenol-betaine constitution, $C_{16}H_{15}O_2{<}^{O}_{N(CH_3)_2}$, was provisionally assigned. Further experiments have demonstrated the correctness of this assumption, for on treatment with methyl iodide, the methiodide of an iso*codeine* was obtained:

$$C_{16}H_{15}O_2{<}^{O}_{N(CH_3)_2} + CH_3I = C_{16}H_{15}O_2{<}^{OCH_3}_{N(CH_3)_2I}$$

According to this equation, the phenolic hydroxyl group of the molecule should become methylated by the action of methyl iodide. That this reaction does in reality take place as shown is evident from

the fact that *iso*codeine methiodide has been obtained by two other methods, namely :

(*a*) By the action of methyl iodide in excess on an alcoholic solution of the sodium derivative of *iso*morphine.

(*b*) Codeine, $C_{17}H_{18}(OCH_3)O_2N$ (the methyl ether of morphine), when treated with phosphorus tribromide, yields a crystalline derivative, $C_{17}H_{17}(OCH_3)ONBr$, which, on treatment with water, decomposes according to the equation :

$$C_{17}H_{17}(OCH_3)ONBr + H_2O = C_{17}H_{18}(OCH_3)O_2N,HBr.$$

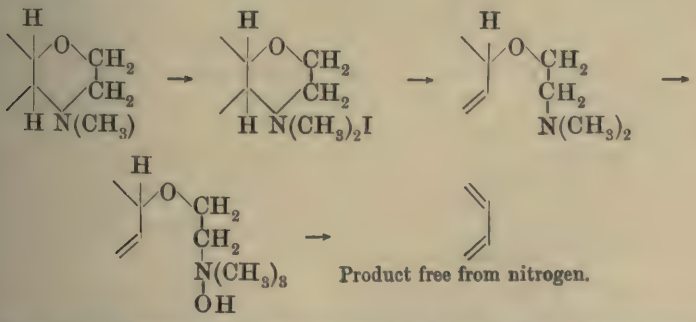
By this means, the hydrobromide of a base isomeric with codeine is obtained, which may be designated iso*codeine*, and this product yields a methiodide identical with that obtained by the two other reactions described above. These reactions prove beyond all doubt the phenol-betaine constitution of *iso*morphine methohydroxide, thus clearly demonstrating an analogy with the corresponding morphine derivative.

When *iso*codeine methiodide is treated with sodium hydroxide, it decomposes according to the equation :

$$C_{16}H_{15}O_2(OCH_3):N(CH_3)_2I + NaOH = NaI + H_2O + C_{16}H_{14}O_2(OCH_3)\cdot N(CH_3)_2.$$

The base thus obtained is designated in this paper *methi*-iso*morphimethine*, and differs from the base methimorphimethine obtained by an analogous reaction from codeine methiodide in that it is slightly dextrorotatory and melts at 167°, whereas methimorphimethine is strongly lævorotatory and melts at 118°. The methohydroxides of both methi-*iso*morphimethine and methimorphimethine, however, yield one and the same nitrogen-free product on heating, namely, morphenol methyl ether, $C_{15}H_{10}O_2$.

These reactions are characteristic of morpholine derivatives, the mechanism of the exhaustive methylation of which may be briefly represented as follows : *



* A more detailed *résumé* of the mechanism of these reactions, as interpreted by Knorr, is given in the introduction to our previous paper.

From the above reactions, a complete analogy between morphine and *iso*morphine is demonstrated, and this can be seen by a glance at the appended table.

Relationship between morphine and iso*morphine.*

	Morphine.		*iso*Morphine.	
	M. p.	$[\alpha]_D$.	M. p.	$[\alpha]_D$.
Base, $C_{17}H_{19}O_3N$	253°	−132·7°	247°	−167°
↓ $[CH_3I]$				
Methiodide, $C_{17}H_{19}O_3N,CH_3I$	279	−73·1	279	−95·2
↓ $[Ag_2SO_4 + Ba(OH)_2]$				
Methohydroxide, $C_{17}H_{19}O_3N,CH_3{\cdot}OH$	phenol-betaine + H_2O		phenol-betaine + H_2O	
↓ $[CH_3I]$				
Codeine methiodide, $C_{18}H_{21}O_3N,CH_3I$	273°	−78·9°	265°	−102·1°
↓ [NaOH]				
Methimorphimethine, $C_{19}H_{23}O_3N$	118	−212	167	+64·6
↓ $[CH_3I]$				
Methimorphimethine methiodide, $C_{19}H_{23}O_3N,CH_3I$	245	−94·5	265	+84·7
↓ [AgOH]				
Methohydroxide, $C_{19}H_{23}O_3N,CH_3{\cdot}OH$	not isolated		not isolated	
↓ [Heat]				
Product free from nitrogen, $C_{15}H_{10}O_2$	morphenol methyl ether, m. p. 65°		morphenol methyl ether, m. p. 65°	

From the facts recorded above, the following conclusions may be drawn:

(I.) *iso*Morphine contains two hydroxyl groups, as evidenced by the fact that it forms a diacetyl derivative, and by other reactions.

(II.) One of these hydroxyl groups is of phenolic character, as is evident from the formation of a phenol-betaine derivative.

(III.) *iso*Morphine contains a morpholine ring, as demonstrated by the products of exhaustive methylation.

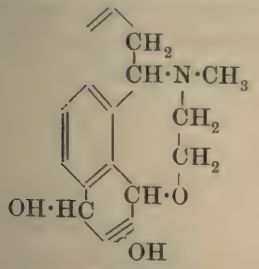
(IV.) The phenanthrene complex exists in *iso*morphine. This is evident from the fact that morphenol methyl ether, the formula of which is discussed below, is formed by the action of heat on the methohydroxide of methi*iso*morphimethine.

These groups are exactly the same as those contained in morphine. The question then remains, In what relation does *iso*morphine stand to morphine? To this problem there seems to be but two possible solutions.

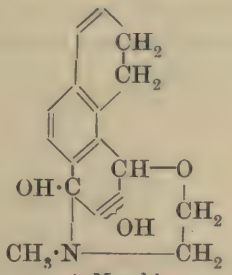
(*a*) *It is possible that morphine and* iso*morphine are stereoisomerides.* If this be the case, the stereoisomerism can have reference to one, and *only one*, of the carbon atoms, namely, that to which the alcoholic hydroxyl group is attached. It has been shown, however, that when bromomorphide is treated with water, *iso*morphine and *β-iso*morphine are obtained, but no morphine. There are, therefore, three isomerides existing, which cannot all be stereoisomeric. It is therefore evident that some other explanation must be sought to account for the isomerism of these three substances, although the possibility of stereoisomerism between any two is not absolutely excluded. Nevertheless, this explanation of the isomerism between morphine and *iso*morphine seems highly improbable, in view of many facts which are not discussed here.

(*b*) The only other possibility is that *either the nitrogen or the oxygen of the morpholine complex is attached to different points of the phenanthrene nucleus* in morphine and *iso*morphine respectively. As the same morphenol methyl ether is obtained from both morphine and *iso*morphine, it is evident that if these bases are structurally different they can only differ in the point of attachment of the morpholine ring, as the latter complex is entirely severed from the molecule in the series of reactions by which morphenol methyl ether is obtained.

It is probable that during the treatment of morphine with phosphorus tribromide a temporary scission of the morpholine ring occurs; such a scission can take place either at the oxygen or nitrogen atom, the latter being the more probable, as several examples of the opening of a saturated ring containing nitrogen are known. Owing to the replacement of a hydroxyl group by a heavy bromine atom, it is possible that the shape of the molecule will be altered, and consequently that a different point of the phenanthrene nucleus having a hydrogen atom attached will stand nearer to the nitrogen atom than the point to which it was previously attached, supposing a scission to have taken place at the latter element. The relationship of morphine and *iso*morphine to one another, according to this hypothesis, may be represented by the two following or analogous formulæ:



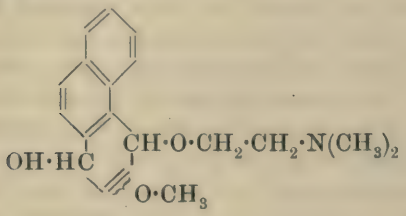
Morphine.*



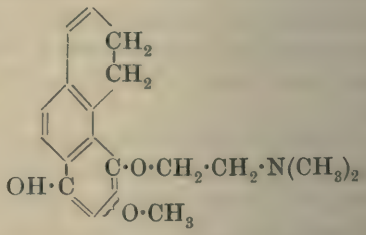
*iso*Morphine.

* Formula suggested by Knorr.

These products would give rise to methimorphimethines of the following constitution :

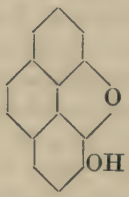


and

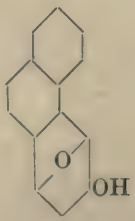


The methohydroxides of the two methimorphimethines having the constitution indicated should, on heating, yield one and the same morphenol methyl ether.

For morphenol, Vongerichten has proposed the following constitution :



Now, since the anhydride oxygen group does not pre-exist in methimorphimethine, which forms an acetyl derivative (Knorr, *Ber.*, 1894, 27, 1149), a morphenol of the above constitution can only be derived from substances having the formulæ given above for morphine and *iso*-morphine by the addition of a hydroxyl group to that point of the phenanthrene nucleus to which the nitrogen atom was originally attached in the morphine molecule. Such an addition seems improbable, and we venture to suggest for morphenol the following alternative formula, which, we believe, explains equally well all the known reactions of this compound :



The experiments recorded in this communication have yielded results of interest from a standpoint other than the purely chemical. The work was originally undertaken to determine the influence of the various subsidiary groups (hydroxyl, &c.) upon the physiological action of morphine. Incidentally a product, *iso*morphine, has been isolated which contains the same groups as morphine, namely, two hydroxyl groups—one of alcoholic, the other of phenolic nature—a morpholine complex and a phenanthrene residue. The two compounds behave chemically in a perfectly analogous manner, yet the one is powerfully narcotic in its action, the other non-narcotic. In reference to this point, attention may be called to the views of P. Ehrlich expressed in an address delivered before the *Verein für innere Medizin*, Dec. 12th, 1898, of which the following is an approximate translation :—"From the results of previous researches, it appears that the most rational method for obtaining substances of therapeutic value is, in the first instance, to discover substances which have an affinity for certain organs (*haptophors*), and then to introduce into these substances groups which are known to exercise a definite therapeutic action (*pharmacophors*)" (*Berliner klinische Wochenschrift*, 1900, **36**, 17). The experimental details upon which the above views are founded are published by Ehrlich mainly in two monographs, "Wertbemessung des Diphtherieheilserums und deren theoretische Grundlagen" (*Abdruck aus dem klinischen Jahrbuch*, Bd. II. G. Fischer, Jena, 1897), and "Das Sauerstoffbedürfniss des Organismus" (Fischer, 1885). In the case of morphine, the recent researches of Knorr have made it extremely probable that the morpholine radicle is the "pharmacophor" group. The "haptophor" group, however, cannot at present be defined, seeing that a seemingly insignificant change in the configuration of the molecule can cause such a marked difference in physiological action. In this connection, it would be of interest to trace out the influence of stereochemical configuration on physiological action, and if a distinct difference were demonstrated between various stereoisomerides, the result would be such as the researches of E. Fischer and others on the sugars and glucosides permit us even now to forecast.

The further investigation of the substances described in this paper is in progress, and it is hoped the results may soon be ready for presentation to the Society.

Experimental.

β-iso*Morphine*.

Separation of iso*Morphine and* β-iso*Morphine*.—For the preparation and separation of these isomeric bases, bromomorphide was treated by a method slightly different from that described in our previous

paper (*loc. cit.*, p. 1035). The method of procedure was as follows. Bromomorphide, in lots of 20 grams, was suspended in 200 c.c. of water contained in a reflux apparatus, and to the slightly warmed mixture just sufficient glacial acetic acid was carefully added to cause the suspended base to dissolve. The solution was vigorously boiled for 3—4 hours, and then evaporated to a syrup on the water-bath. After several successive additions of alcohol and subsequent evaporation, this syrup formed a crystalline paste, which was drained by the aid of a filter pump: the crystalline salt, after being washed with alcohol until white, was allowed to dry by spreading it on a porous plate. The total amount of alkaloidal salt obtained was only equivalent to somewhat more than 50 per cent. of that theoretically possible. The mother liquor, after further concentration, yielded a very dark coloured syrup, from which no further amount of crystalline product could be obtained.

For conversion into base, the salt, in lots of 10—15 grams, was dissolved in 100 c.c. of water contained in a separating funnel; the solution was covered with a layer of pure ether, and rendered alkaline by the addition of 40 c.c. of a saturated solution of sodium carbonate, when the liberated base at first separated and then on shaking went into solution again. On standing, however, it separated in a beautifully crystalline form. As no further separation of crystalline base occurred after standing for 24 hours, the layer of ether, which was found to contain only a small amount of colouring matter, was separated from the alkaline aqueous liquid containing the crystalline base in suspension. The base was collected by filtration at the pump, washed, first with a little water, then with alcohol, and finally recrystallised from absolute alcohol, from which it separated in clusters of prismatic needles; these melted at 247° with slight decomposition, and in methyl alcoholic solution had the specific rotation $[\alpha]_D = -166{\cdot}5°$. The product thus obtained (22 grams of base from 45 grams of the alkaloidal salt) was homogeneous and in all respects identical with *iso*morphine as obtained from bromomorphide according to the method described in our previous paper.

As the amount of crystalline base thus obtained did not account for the whole of the alkaloidal salt employed, it was obvious that the alkaline aqueous filtrate from the *iso*morphine still contained a quantity of base in solution, and in order to obtain this the solution was extracted with hot amyl alcohol until the aqueous liquid was free from organic base, as was shown by acidifying a portion with hydrochloric acid and adding Mayer's reagent. The amyl alcoholic solution was washed once with a little water, and then extracted four times with dilute hydrochloric acid. The acid aqueous solution of the hydrochloride of the extracted base was evaporated to a low bulk, and after

several additions of alcohol, further evaporated, when suddenly the whole formed a crystalline cake; this was mixed with alcohol and collected at the pump. The crystalline hydrochloride thus obtained weighed 8 grams when dry; it was recrystallised from water and separated in rounded clusters of prismatic needles. On determining its specific rotation in aqueous solution, the following result was obtained:

$$\alpha_D = -4°32'; \; l = 1 \text{ dcm.}; \; c = 2·257; \; [\alpha]_D^{11°} = -200·8°.$$

The aqueous mother liquor from the recrystallised salt was distilled with several additions of alcohol in order to eliminate the greater portion of the water, and a solution in alcohol was thus obtained from which the salt easily crystallises almost in its entirety. This further crop of crystalline product was collected, dried, and its specific rotation determined, with the following result:

$$\alpha_D = -2°40'; \; l = 1 \text{ dcm.}; \; c = 1·358; \; [\alpha]_D^{17°} = -196·4°.$$

It is thus apparent from these numbers that this hydrochloride is a homogeneous product, and that it differs from the hydrochlorides of either *iso*morphine or morphine, which have respectively the specific rotations $[\alpha]_D^{20°} = -150°$ and $-111·5°$.

Analyses of the hydrochloride recrystallised from water and (i) dried in the steam oven, (ii) dried in the air, were made, with the following results:

0·1542 gave 0·3608 CO_2 and 0·0895 H_2O. C = 63·8; H = 6·4.
0·1272 „ 0·2974 CO_2 „ 0·074 H_2O. C = 63·7; H = 6·5.
$C_{17}H_{19}O_3N,HCl$ requires C = 63·5; H = 6·2 per cent.

β-iso*Morphine* was obtained from the hydrochloride by suspending it in alcohol, and slowly adding a dilute solution in alcohol of one atomic equivalent of sodium. The hydrochloride quickly dissolved, and after removal of the sodium chloride, the alcoholic solution was concentrated, filtered from a further small amount of sodium chloride which had separated, and somewhat further concentrated, when a glistening, crystalline base was deposited. This was collected and recrystallised from hot alcohol, in which it is only moderately soluble, and from which it separates in well-defined, double, rhombic pyramids. When heated in a capillary tube, the base assumed a softened appearance at 145—150°, but was otherwise permanent until 182°, when it melted sharply without decomposition, and this behaviour on heating was not altered after the base had been recrystallised several times from alcohol. On analysis, the following numbers were obtained:

0·1755 gave 0·447 CO_2 and 0·1115 H_2O. C = 69·5; H = 7·1.

In view of the singular behaviour of this base on heating, and of

the fact that the analytical numbers are not in agreement with those required for the formula $C_{17}H_{19}O_3N$, the presence of alcohol of crystallisation was suspected. Examination showed that when the crystalline base, previously dried in the steam oven, was heated in an open test-tube to a temperature somewhat above its melting point, alcohol was evolved, which could be ignited at the mouth of the tube. After the evolution of alcohol had ceased, the substance was allowed to cool, when it soon set to a hard, light brown resin; this was powdered, dissolved in hot alcohol with the addition of a little animal charcoal, and the solution filtered while hot, when crystals soon separated, which were collected and found to exhibit the same behaviour with respect to melting point as the base did before heating. On analysis, the following numbers were obtained:

0·1529 gave 0·3924 CO_2 and 0·0982 H_2O. C = 70·0; H = 7·1.
0·6833, heated at 120°, lost 0·0513 C_2H_6O. C_2H_6O = 7·5.
$(C_{17}H_{19}O_3N)_2,C_2H_6O$ requires C = 70·1; H = 7·1; C_2H_6O = 7·4 per cent.

Analysis of base free from alcohol:

0·1231 gave 0·3232 CO_2 and 0·0778 H_2O. C = 71·6; H = 7·0.
$C_{17}H_{19}O_3N$ requires C = 71·6; H = 6·7 per cent.

The base when free from alcohol melted sharply at 182°. A determination of the specific rotation in methyl alcoholic solution of the base containing $\frac{1}{2}$-mol. of alcohol of crystallisation gave the following result:

$$\alpha_D = -3°32'; \; l = 1 \text{ dcm.}; \; c = 1·634; \; [\alpha]_D^{17°} = -216·2°.$$

*β-iso*Morphine is sparingly soluble in cold, but somewhat more readily in hot, alcohol; it is almost insoluble in ether or light petroleum, but readily soluble in hot acetone, benzene, or chloroform; it also dissolves easily in water, forming a strongly alkaline solution, which almost immediately reduces silver salts.

The *methiodide* was prepared in the usual way. On recrystallisation from water, from which it separated in glistening tablets, it melted at 250° with only slight decomposition. On analysis, the following numbers were obtained:

0·1284 gave 0·2344 CO_2 and 0·0627 H_2O. C = 49·8; H = 5·4.
0·4823 required 11·4 c.c. $N/10$ $AgNO_3$ solution. I = 30·0.
$C_{17}H_{19}O_3N,CH_3I$ requires C = 50·6; H = 5·1; I = 29·8 per cent.

A determination of the specific rotation in aqueous solution gave the following result:

$$\alpha_D = -3°11'; \; l = 1 \text{ dcm.}; \; c = 2·178; \; [\alpha]_D^{23°} = -146·1°.$$

Reactions of iso*Morphine.*

*Diacetyl*isomorphine *Methiodide*, $C_{17}H_{17}O_3N(CO{\cdot}CH_3)_2,CH_3I$.—*iso*-Morphine (2 grams) was dissolved in acetic anhydride (10 grams) and the solution warmed on the water-bath for 2 days. The product was then mixed with water (100 c.c.), and allowed to stand until all the acetic anhydride had dissolved, when the solution was rendered strongly alkaline with sodium carbonate. A base separated which was readily taken up by pure ether. The ethereal solution, after washing once with water, was dried over calcium chloride and the ether distilled off. The residual, light yellow syrup, even after many successive heatings to 100°, and subsequent standing in an exhausted desiccator, showed, however, no signs of crystallising, but when dissolved in alcohol, mixed with excess of methyl iodide, and the mixture boiled, a beautifully crystalline methiodide was precipitated. This was collected, dissolved in hot methyl alcohol, and the solution allowed to stand, when almost immediately the methiodide separated in well-formed, silky needles which melted at 241—242° with some decomposition. On analysis, the following numbers were obtained :

0·1494 gave 0·2815 CO_2 and 0·0786 H_2O. C = 51·4 ; H = 5·8.
$C_{22}H_{26}O_5NI$ requires C = 51·6 ; H = 5·1 per cent.

Action of Phosphorus Tribromide.—When *iso*morphine (3 grams) was added to a solution of phosphorus tribromide (3 grams) in chloroform (10 grams), and the mixture boiled in a reflux apparatus on the water-bath, interaction quickly ensued with some evolution of hydrogen bromide. The heating was continued for 7 hours, when the product, in the form of a gelatinous hydrobromide, formed a layer under the chloroform. Alcohol was added in order to decompose the excess of phosphorus bromide, the resulting clear, light yellow solution mixed with an equal volume of water, and the whole made alkaline with sodium carbonate and extracted five times with pure ether. The ethereal solution was washed with water and shaken out with dilute hydrobromic acid, when almost immediately the aqueous layer deposited a sparingly soluble hydrobromide. This was collected and recrystalled from hot water, in which it was only sparingly soluble, and from which it separated in beautiful, glistening, prismatic needles. The very moderate solubility of this hydrobromide, and its crystalline form, suggested at once that it was the hydrobromide of bromomorphide, which, as described in our previous communication (*loc. cit.*, p. 1032), can be formed from morphine by the action of phosphorus tribromide. This was found to be the case, for when the hydrobromide was redissolved in water, the solution made alkaline with sodium carbonate, extracted

with ether, and the ethereal solution dried and concentrated, a white, sandy, crystalline base was deposited, which proved to be bromomorphide, as it melted at 170° with decomposition, and in methyl alcoholic solution had a specific rotation of +68°.

$$\alpha_D = +2°36'\ ;\ l = 2\ \text{dcm.}\ ;\ c = 1{\cdot}898\ ;\ [\alpha]_D = +68°.$$

Action of Hydrobromic Acid.—As might be expected from the result of the last experiment, *iso*morphine, like morphine (compare previous paper, *loc. cit.*, p. 1034), when treated with hydrobromic acid, yielded bromomorphide.

Action of Phosphorus Trichloride.—*iso*Morphine (5 grams) was treated with phosphorus trichloride in a manner exactly analogous to that described for morphine in our previous paper (*loc. cit.*, p. 1029), and the resulting light brown varnish disintegrated with iced water. The acid aqueous solution, made strongly alkaline with sodium carbonate, was extracted six times with chloroform, this chloroform solution washed with water, dried over calcium chloride, and the solvent distilled off. A small amount of a yellow syrup was obtained which showed no signs of crystallising even after long standing, but seemed to decompose readily when any attempt was made to form a methiodide. Its solution in organic solvents seemed to undergo oxidation readily, giving coloured solutions not dissimilar to those given by apomorphine under the same conditions. Although this reaction was carried out several times and under varying conditions, in no case could any chloromorphide be isolated from the products of the reactions, thus showing that *iso*morphine does not resemble morphine in its behaviour with phosphorus trichloride.

iso*Codeine Methiodide.*

iso*Codeine Methiodide*, $C_{17}H_{18}O_2N(OCH_3),CH_3I$, was prepared by the three following methods.

(*a*) *From* iso*Morphine Methiodide.*—To a solution of methiodide (5·6 grams) in hot water (150 c.c.) was added a hot aqueous solution of silver sulphate (2·1 grams = 1½ mol.). Double decomposition immediately ensued with precipitation of silver iodide, which was separated by filtration at the pump, after the mixture had been boiled for some minutes. To the hot filtrate an aqueous solution of barium hydroxide [2·5 grams $Ba(OH)_2,8H_2O = \frac{1}{2}$ mol.] was added, the mixture heated to boiling, and carbon dioxide passed through for some minutes to precipitate any slight excess of barium. After filtration from barium sulphate, the clear, strongly alkaline, aqueous solution of the basic hydroxide was concentrated to 50 c.c. on the water-bath, and then placed in an exhausted desiccator over sulphuric acid. In this way, a light brown, solid cake was formed, which was readily powdered.

This substance was extremely soluble in water, giving a strongly alkaline solution, which proved to be free from silver, iodine, sulphuric acid, and barium. The powdered substance was dissolved in hot methyl alcohol, excess of methyl iodide added, the solution boiled for half an hour on the water-bath, and then concentrated, when a beautifully crystalline methiodide separated. This was collected and dissolved in hot methyl alcohol, in which it was easily soluble, but separated readily on cooling in the form of glistening leaflets melting at 262° with decomposition. On analysis, the following results were obtained:

0·1614 gave 0·3042 CO_2 and 0·0826 H_2O. C = 51·4; H = 5·7.
0·4529 required 10·4 c.c $N/10$ $AgNO_3$ solution. I = 29·1
$C_{19}H_{24}O_3NI$ requires C = 51·7; H = 5·5; I = 28·8 per cent.

A determination of the specific rotation in aqueous solution gave the following result:

$$\alpha_D = -2°30'; \; l = 1 \text{ dcm.}; \; c = 2·504; \; [\alpha]_D^{17°} = -99·8°.$$

*iso*Codeine methiodide is nearly insoluble in hot ethyl alcohol, but readily soluble in hot water, and on concentrating the solution, separates in a beautifully crystalline form. When its solution in dilute sodium hydroxide is boiled for two minutes, the clear liquid quickly becomes clouded with oily drops, soon solidifying to a crystalline mass, which, after recrystallisation from alcohol, melts at 167°. The preparation of this base from *iso*codeine methiodide is described in detail on p. 577.

(*b*) *By the action of Sodium Ethoxide and Methyl Iodide on* iso*Morphine.*—*iso*Morphine (5·25 grams) was suspended in ethyl alcohol, and a solution of sodium (0·42 gram = 1 atomic proportion) in alcohol slowly added, with shaking. The *iso*morphine went into solution, forming a sodium derivative. Methyl iodide (10 grams) was then added, and the solution boiled for 20 minutes, when suddenly a crystalline methiodide separated in quantity. This was collected and found to melt at 265°, with decomposition. A determination of the specific rotation in aqueous solution gave the following result:

$$\alpha_D = -2°27'; \; l = 1 \text{ dcm.}; \; c = 2·40; \; [\alpha]_D^{17°} = -102·1°.$$

This methiodide was in all respects identical with the one prepared by method (*a*), yielding, on boiling its aqueous solution with sodium hydroxide, the base melting at 167°.

(*c*) *From Codeine. Bromocodeide,* $C_{18}H_{20}O_2NBr$.—Codeine dried at 100° (24 grams) was dissolved in chloroform (60 grams) contained in a reflux apparatus, and phosphorus tribromide (24 grams), dissolved in about an equal weight of chloroform, was added. Immediate interaction took place with development of heat and evolution of some

hydrogen bromide, and after a time a gelatinous hydrobromide separated from the solution. The whole was boiled for an hour, cooled, mixed with an equal bulk of alcohol in order to decompose any excess of phosphorus bromide, thrown into water, rendered alkaline with sodium carbonate, and extracted six times with a chloroform-ether mixture. The chloroform-ether solution of the base, after washing four times with water, was dried over calcium chloride and the chloroform-ether distilled off, when a light yellow oil remained which almost immediately began to crystallise, and soon set to a hard, crystalline cake. This was ground up and recrystallised from ethyl alcohol, in which it is readily soluble while hot, but only sparingly so in the cold; it separates in the form of beautiful, highly refractive, pearly scales, melting at 162° to a faintly reddish-coloured liquid.

On analysis, the following results were obtained:

0·1382 gave 0·3059 CO_2 and 0·0712 H_2O. C = 60·4; H = 5·7.
0·3408 „ 0·1758 AgBr. Br = 21·9.
$C_{18}H_{20}O_2NBr$ requires C = 59·7; H = 5·5; Br = 22·1 per cent.

A determination of the specific rotation in ethyl alcohol gave the following result:

$$\alpha_D = +1°4'; \; l = 1 \text{ dcm.}; \; c = 1·887; \; [\alpha]_D^{20°} = +56·5°.$$

The yield of bromocodeide, prepared as above, is almost quantitative.

iso*Codeine*, $C_{17}H_{18}O_2N(OCH_3)$.—This was obtained from bromocodeide by the action of water, as follows. Bromocodeide (20 grams) was suspended in water (200 c.c.) contained in a reflux apparatus, and to the warmed mixture glacial acetic acid was added, drop by drop, until the suspended base just dissolved. The clear solution so obtained was boiled for 3 hours, cooled, made alkaline with sodium carbonate, and the base which separated taken up by ether. The ethereal solution was washed with a little water, dried, and concentrated, when on standing a short time a crystalline base melting at 140—144° separated out. This was collected and recrystallised twice from pure dry ether by extraction in a Soxhlet apparatus. The base separates from boiling ether in beautiful, long, prismatic needles, which are quite free from bromine and melt at 144°. It is very easily soluble in cold methyl or ethyl alcohol, and can be readily recrystallised by dissolving in a small amount of the former solvent and distilling with repeated additions of dry ether.

A specimen of the base recrystallised from ether was analysed, with the following results:

0·1775 gave 0·4737 CO_2 and 0·1152 H_2O. C = 72·7; H = 7·2.
$C_{18}H_{21}O_3N$ requires C = 72·3; H = 7·0 per cent.

A determination of the specific rotation in methyl alcoholic solution gave the following result:

$$\alpha_D = -4°2'\ ;\ l = 1 \text{ dcm.}\ ;\ c = 2{\cdot}384\ ;\ [\alpha]_D^{18°} = -169{\cdot}1°.$$

There were indications that another base of somewhat higher melting point than *iso*codeine had been formed, together with the latter, during the decomposition of bromocodeide with water; it was present, however, in such small amount that we were unable to isolate anything definite. It might be noted that codeine melts at 156—157°; is sparingly soluble in cold ethyl alcohol, and has a much lower specific rotation than *iso*codeine.

iso*Codeine methiodide* was prepared in the usual way, and as it became slightly coloured with iodine during drying, it was recrystallised from hot methyl alcohol, from which it separated in beautiful, glistening crystals melting at 262° with decomposition. A determination of its specific rotation gave the following result:

$$\alpha_D = -2°30'\ ;\ l = 1 \text{ dcm.}\ ;\ c = 2{\cdot}488\ ;\ [\alpha]_D^{14°} = -100{\cdot}5°.$$

It is thus seen that these constants are the same as those determined for the methiodides prepared by methods (*a*) and (*b*), and this, together with the fact that the methiodide last mentioned yielded the base melting at 167° on treatment with sodium hydroxide, proved in a marked manner the complete identity of the substances prepared by the three methods.

Action of Sodium Hydroxide on iso*Codeine Methiodide.*

Methi-iso*morphimethine*, $C_{18}H_{20}O_2N(OCH_3)$.—*iso*Codeine methiodide (5 grams) was dissolved in hot water (25 c.c.), and a 25 per cent. solution of sodium hydroxide (6 c.c.) added. The clear solution was boiled for 2 minutes, when suddenly it became cloudy owing to the separation of an oil; the boiling was continued for 10 minutes and the mixture cooled, when the oil formed a light yellow syrup on the bottom of the flask, and after a short time solidified to a white, crystalline cake. This was separated from the mother liquor, ground up with alcohol, collected at the pump, allowed to drain on a porous plate, and finally recrystallised from ethyl alcohol, from which it separated in beautiful transparent tablets melting at 167°. On analysis, the following results were obtained:

0·1823 gave 0·4876 CO_2 and 0·1225 H_2O. C = 72·9; H = 7·5.

$C_{19}H_{23}O_3N$ requires C = 72·8; H = 7·3 per cent.

A determination of the specific rotation in chloroform solution gave the following result:

$$\alpha_D = +2°\ ;\ l = 1 \text{ dcm.}\ ;\ c = 3{\cdot}094\ ;\ [\alpha]_D^{20°} = +64{\cdot}6°.$$

Methi-*iso*morphimethine is a base and readily forms salts, the hydrochloride separating from water in a beautifully crystalline form. It is only soluble in large quantities of hot ethyl or methyl alcohol, and crystallises well from either. On making aqueous solutions of its salts alkaline, it can readily be extracted by ether.

Methi-isomorphimethine Methiodide, $C_{18}H_{20}O_2N(OCH_3),CH_3I$, was prepared in the usual way by dissolving the base in hot ethyl alcohol, and adding a weight of methyl iodide equal to that of the base taken. Almost immediately after mixing, the methiodide separated from the hot solution in the form of beautiful, long, white needles melting at 265° with slight decomposition. On analysis, the following result was obtained:

0·516 required 11·4 c.c. $N/10$ $AgNO_3$ solution. I = 28·05.
$C_{20}H_{26}O_3NI$ requires I = 27·91 per cent.

A determination of the specific rotation in aqueous solution gave the following result:

$$\alpha_D = +1°5'; \; l = 2 \text{ dcm.}; \; c = 1·56; \; [\alpha]_D^{17°} = +34·7°.$$

Action of Heat on Methi-isomorphimethine Methohydroxide.

Methi-*iso*morphimethine methiodide (9·7 grams) was dissolved in hot water (100 c.c.), and to the hot solution silver hydroxide, freshly precipitated from an aqueous solution of silver nitrate (3·8 grams), and subsequently well washed with water, was added. Immediate double decomposition ensued, with formation of silver iodide and the hydroxide of the base. The mixture was allowed to stand for 12 hours, when the silver iodide was filtered off, and the clear, strongly alkaline filtrate rapidly evaporated over a free flame to a small bulk. As no evolution of any of the lower fatty amines took place during this concentration, the dark brown syrup was introduced into a 150 c.c. flask and heated in an oil-bath at 160—170°, when bases smelling of ammonia were evolved, and the substance in the flask frothed somewhat. It soon, however, became tranquil, ceased to evolve amines, and, on cooling, set to a hard mass. Pure ether was added, the mixture boiled for some hours, the ethereal extract filtered from a large amount of carbonaceous matter formed during the reaction, and the ether distilled off. The residue was a fluorescent, light brown oil, which quickly solidified to a crystalline mass. This was easily purified by twice recrystallising from ethyl alcohol, from which it separated in highly lustrous, prismatic needles melting sharply at 65°. It contained no nitrogen, and was analysed, with the following results:

0·1666 gave 0·4942 CO_2 and 0·0686 H_2O. C = 80·9; H = 4·6.
$C_{15}H_{10}O_2$ requires C = 81·1; H = 4·5 per cent.

This substance is therefore *identical with the morphenol methyl ether* (m. p. 65°) obtained by Knorr by an analogous series of reactions from morphine (*Ber.*, 1889, **22**, 183).

Action of Water on Chloromorphide.

Chloromorphide (20 grams) was suspended in water (200 c.c.), and glacial acetic acid added carefully to the slightly warmed mixture until the base had all entered into solution. The liquid was boiled in a reflux apparatus for 4 hours, and then evaporated to a small bulk. The light yellow syrup, after successive additions of alcohol and further evaporation, soon set to a crystalline cake, which was ground up with alcohol and the whole thrown on to a filter and drained at the pump. As in the case of the action of water on bromomorphide (compare p. 570), the alcoholic mother liquor contained a considerable quantity of uncrystallisable product, but notwithstanding this the yield of white hydrochloride amounted to 50—60 per cent. of the theoretical. On determining the specific rotation of this salt in aqueous solution, the following result was obtained:

$$\alpha_D = -4°48'\ ;\ l = 2 \text{ dcm.}\ ;\ c = 2{\cdot}087\ ;\ [\alpha]_D^{21} = -115°.$$

The hydrochloride (10 grams) was then dissolved in water (100 c.c.) contained in a separating funnel, and 40 c.c. of a saturated solution of sodium carbonate were added; a white, amorphous base separated, which readily dissolved in the excess of sodium carbonate employed. The clear, alkaline liquid was then extracted ten times with chloroform, the chloroform solution washed once with a little water, dried over calcium chloride, and the chloroform distilled off. The residue consisted of a light brown oil which soon set to a varnish. The alkaline aqueous liquid was further extracted with chloroform until, on distilling off the latter, no more of the varnish was obtained. This base was readily dissolved by hot ethyl alcohol, and the solution, after boiling with a little animal charcoal, filtering, concentrating, and standing a short time, deposited a mass of glistening crystals, which was collected and recrystallised from ethyl alcohol. This crystalline base so obtained had all the properties of *β-iso*morphine, obtained, together with *iso*morphine, by the action of water on bromomorphide, as described on p. 571; it melted in an identical manner. On analysis, the following results were obtained:

0·1564 gave 0·3998 CO_2 and 0·0992 H_2O. C = 69·7; H = 7·0.

$(C_{17}H_{19}O_3N)_2,C_2H_6O$ requires C = 70·1; H = 7·1 per cent.

A determination of the specific rotation in methyl alcoholic solution gave the following result:

$$\alpha_D = -3°22'\ ;\ l = 1 \text{ dcm.}\ ;\ c = 1{\cdot}556\ ;\ [\alpha]_D^{19°} = -216{\cdot}3°.$$

The alkaline aqueous solution from which all the *β-iso*morphine had been extracted by chloroform was then shaken out with successive amounts of hot amyl alcohol, until the aqueous portion, after acidifying, showed no reaction on the addition of Mayer's reagent. The amyl alcoholic solution, after washing once with a little water, was extracted several times with dilute hydrochloric acid, and the acid aqueous solution of the hydrochloride evaporated to a small bulk, alcohol added, and the evaporation continued. This addition of alcohol, followed by evaporation, was repeated several times, when the hydrochloride was obtained as a crystalline cake which, after mixing with more alcohol, was drained and washed at the pump. The salt was then dissolved in water, from which solvent it crystallised. Two fractions of crystalline hydrochloride obtained from water, on determining their specific rotations in aqueous solution, gave the following results respectively:

$$\alpha_D = -4°4'\ ;\ l=2 \text{ dcm.}\ ;\ c=2{\cdot}17\ ;\ [\alpha]_D = -94°.$$
$$\alpha_D = -3°51'\ ;\ l=2 \text{ dcm.}\ ;\ c=2{\cdot}081\ ;\ [\alpha]_D = -92{\cdot}5°.$$

It would thus seem as if this were a pure hydrochloride of a base which has not hitherto occurred during the course of this work. Its further investigation, together with that of *β-iso*morphine, will, however, form the subject of a future communication.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES.

LXII.—*The Constitution of Pilocarpine. Part II.*

By HOOPER ALBERT DICKINSON JOWETT, D.Sc.

IN former papers (this Journal, 1900, **77**, 494, 851), it was shown that the nitrogen atoms occur in *iso*pilocarpine as :NH and :NCH_3, and that when oxidised with permanganate, an acid of the formula $C_7H_{10}O_4$ is produced. The constitutional formula,

$$(CH_3)_2CH\cdot CH\cdot CH\cdot CO_2H$$
$$\qquad\qquad\quad O—CO \qquad ,$$

was provisionally assigned to this acid, but as it is at present under investigation, and as frequent reference has to be made to it in this paper, the name of *pilopic acid* is proposed for it. The present paper deals with experiments on pilocarpine and *iso*pilocarpine, chiefly on the latter, as it is the more stable of the two alkaloids, and it was thought that the nature of the isomerism could be more conveniently studied when the constitution of the more stable isomeride had been determined. By the action of bromine on *iso*pilocarpine under varying conditions, several new products have been obtained. *Dibromoiso-*

pilocarpine, $C_{11}H_{14}O_2N_2Br_2$, is obtained as the first and principal product of the interaction of bromine and *iso*pilocarpine at the ordinary temperature. When the reaction is carried out in acetic acid solution, small quantities of an acid, probably iso*pilocarpinic acid*, $C_{11}H_{16}O_4N_2$, are formed, together with a very small quantity of *monobromo*iso*pilocarpine*, $C_{11}H_{15}O_2N_2Br$. Dibromo*iso*pilocarpine is a very feeble base, does not react with methyl iodide, and on reduction yields *iso*pilocarpine quantitatively, identical in all respects with the parent base. On oxidation with permanganate, it yields methylamine, a little ammonia, pilopic acid, and a new crystalline acid, *pilopinic acid*, $C_8H_{11}O_4N$. On further oxidation, the latter acid yields ammonia and pilopic acid.

When bromine acts on *iso*pilocarpine in aqueous solution at 100° in a sealed tube, two chief products are formed, *dibromo*iso*pilocarpinic acid*, $C_{11}H_{14}O_4N_2Br_2$, and *monobromo*iso*pilocarpinic acid*, $C_{11}H_{15}O_4N_2Br$, the former being a well-defined, crystalline acid, whilst the latter has only been obtained as an impure oil. Both these acids, on reduction with zinc and glacial acetic acid, yield the same product, iso*pilocarpinolactone*, $C_{11}H_{14}O_4N_2$. This substance, obtained in well-defined crystals, is a neutral lactone, and with barium hydroxide yields the barium salt of hydroxy*iso*pilocarpinic acid. It possesses one remarkable character, namely, it is non-basic; it can be recrystallised from hot dilute acids, and does not unite with methyl iodide even at 100°. When dibromo*iso*pilocarpinic acid is reduced in alcoholic solution with sodium amalgam, the molecule is broken down and pilopic acid is formed. Dibromopilocarpine has been further studied, and it has been found, contrary to the statements of Pinner and Kohlhammer (*Ber.*, 1900, **33**, 1424), who first prepared this substance, that, like its isomeride, dibromo*iso*pilocarpine, it is very feebly basic and does not unite with methyl iodide. On reduction, it yields pilocarpine quantitatively, identical in all respects with the parent base. Experiments made to prepare bromocarpinic acid, first described by the above-mentioned authors, proved unsuccessful, and the amorphous acids, obtained by the action of bromine on pilocarpine at 100° in aqueous solution and in a sealed tube, yielded, on reduction, an amorphous acid which was certainly not carpinic acid, but probably pilocarpinic acid, $C_{11}H_{16}O_4N_2$.

In addition to the description, mode of preparation, &c., of the above-mentioned new substances, a number of experiments are recorded, in many cases with negative results, but which have an important bearing on the constitution of the alkaloid.

It is shown that *iso*pilocarpine is unaffected by reducing agents such as sodium in boiling amyl alcoholic solution or concentrated hydriodic acid at 127°, and does not exhibit the characteristic

behaviour of an unsaturated compound towards bromine or a saturated solution of hydrogen bromide in glacial acetic acid. The base is also remarkably stable towards chromic acid; action takes place only on prolonged heating, and no crystalline substance has been isolated from the product. Finally, although a full discussion of these results is reserved for a future communication, some of the more important theoretical points of interest are alluded to at the conclusion of this paper.

Action of Bromine on iso*Pilocarpine.*

(1) *In Acetic Acid Solution.*—When bromine acts upon *iso*pilocarpine at the ordinary temperature, dibromo*iso*pilocarpine, $C_{11}H_{14}O_2N_2Br_2$, is the chief product of the reaction; the experiment is best carried out in an acetic acid solution in a manner similar to that described by Pinner and Kohlhammer (*loc. cit.*) for the preparation of dibromopilocarpine. When solutions of bromine and *iso*pilocarpine in 80 per cent. acetic acid are mixed, an oily precipitate is formed which, however, quickly dissolves, and, on standing, the crystalline dibromo-*iso*pilocarpine perbromide separates in brownish needles. By the addition of water to the mother liquor, a further crop of crystals is obtained, but in most cases it was noted that the yield was only 60 per cent. of the theoretical, so the mother liquor from the crystals was further examined to discover the cause of the deficiency. The mother liquors, from which excess of bromine had been removed by long standing, either in the air or over caustic alkali, were extracted several times with ether, the ether then removed by distillation, and the residue boiled with water until all the acetic acid had been driven off. By this method, an oily acid residue was obtained, readily soluble in ether, alcohol, or benzene, but only sparingly so in water. After long standing in a vacuum over sulphuric acid, a solid varnish was obtained which could not be crystallised. It was therefore converted into the barium salt by adding water and boiling with excess of barium carbonate, filtering, and evaporating the solution to a low bulk. The barium salt was then precipitated with absolute alcohol, and was obtained as a microcrystalline powder which contained no bromine, and was analysed, with the following results:

0·0926 gave 0·0358 $BaSO_4$. Ba = 22·7.
0·131 „ 10 c.c. moist nitrogen at 20° and 766 mm. N = 8·6.
$(C_{11}H_{15}O_4N_2)_2Ba$ requires Ba = 22·3; N = 9·1 per cent.

The acid liquid, after extraction with ether, was rendered alkaline with ammonia and shaken several times with chloroform. After removing the chloroform by distillation, a small quantity of a neutral

crystalline substance was obtained. It was purified by repeated crystallisation from alcohol until of constant melting point, and then melted sharply at 164° (corr.). The quantity obtained was too small to admit of a complete analysis, but it was found to contain bromine and nitrogen. On analysis, the following results were obtained:

0·0276 gave 0·046 CO_2 and 0·0132 H_2O. C = 45·4; H = 5·3.
$C_{11}H_{15}O_2N_2Br$ requires C = 45·9; H = 5·2 per cent.

From these results, it would appear almost certain that this substance is *monobromoisopilocarpine*.

The alkaline liquid, after extraction with chloroform, was acidified with sulphuric acid, and then boiled to remove all acetic and hydrobromic acids. It was neutralised with caustic potash, evaporated to dryness, and extracted with absolute alcohol. A slight excess of sulphuric acid was next added to the alcoholic extract, and the precipitated potassium sulphate removed by filtration. Water was added to the alcoholic filtrate, the alcohol removed by evaporation, the aqueous solution boiled with excess of barium carbonate, and the barium salt separated from the filtrate by evaporation and precipitation with alcohol. This barium salt contained no bromine, and on analysis furnished the following results:

0·113 gave 0·1648 CO_2 and 0·05 H_2O. C = 39·8; H = 4·9.
0·0942 ,, 7 c.c. moist nitrogen at 20° and 756 mm. N = 8·3
0·1072 ,, 0·0418 $BaSO_4$. Ba = 22·93.
0·0956 ,, 0·0364 $BaSO_4$. Ba = 22·40.
$(C_{11}H_{15}O_4N_2)_2Ba$ requires C = 42·9; H = 4·9; Ba = 22·3; N = 9·1 per cent.

The low percentage of carbon found might be due to the difficulty of burning a barium salt in an open tube, and to the presence of slight impurity in the material burnt. The yield of these bye-products was so small, and the difficulty of isolating the pure acid so great, that the investigation was not further pursued on these lines. Although the acid could not be obtained in crystalline form and its character determined, yet the results of the analyses indicate that only one acid, *iso*pilocarpinic acid, $C_{11}H_{16}O_4N_2$, is present. Further, the method of preparation, and the close agreement of the analytical numbers of three of the constituents with that required by theory, justify the assumption that the acid is sufficiently pure to assign the above formula to it.

The action of bromine on *iso*pilocarpine in acetic acid solution is therefore one mainly of substitution, with the formation of dibromo-*iso*pilocarpine and a very small quantity of monobromo*iso*pilocarpine, but at the same time a small proportion of the *iso*pilocarpine is oxidised to *iso*pilocarpinic acid.

(2) *In Chloroform Solution.*—When chloroform solutions of bromine and *iso*pilocarpine are mixed, a thick, red oil separates, which does not readily crystallise. By the addition of ammonia to this oil, decolorisation takes place, and a white, crystalline substance is obtained which, on examination, proved to be dibromo*iso*pilocarpine.

Even when a small amount of bromine was added to *iso*pilocarpine, dibromo*iso*pilocarpine was obtained, and monobromo*iso*pilocarpine could not be isolated by this method.

(3) *In Aqueous Solution.*—When bromine water is added to an aqueous solution of *iso*pilocarpine, the colour is instantly discharged, and dibromo*iso*pilocarpine separates as a white, crystalline precipitate. A good yield of the latter substance can be obtained by this method, but it is not so convenient as that previously described. When excess of bromine was added, and the solution boiled to remove bromine, no crystals separated on cooling, but after extracting the acid liquid with ether and removing the ether by distillation, an oily acid was obtained which did not crystallise even after long standing.

The barium salt, prepared in the usual manner with barium carbonate, was found on analysis to contain 24·8 per cent. of barium and 14·45 per cent. of bromine. These figures do not agree with those required for any likely formula for the acid, so the substance was probably a mixture.

(4) *In Aqueous Solution at* 100° *under pressure.*—When bromine is added to an aqueous solution of *iso*pilocarpine, and the mixture heated in a sealed tube at 90—140° for some hours, the dibromo*iso*pilocarpine first produced is oxidised to several acids. The reaction is best carried out as follows. 3·5 grams of *iso*pilocarpine were dissolved in 40 c.c. of water, 2·5 grams of bromine added, and the mixture heated in a sealed tube for 6 hours at 100°. The contents of the tube were then evaporated on the water-bath to remove bromine, and on cooling, crystals of *dibromoisopilocarpinic acid*, $C_{11}H_{14}O_4N_2Br_2$, separated. The acid liquor, after filtration, was then extracted several times with ether, and, after distillation, the ethereal extract yielded a syrupy acid residue consisting chiefly of *monobromoisopilocarpinic acid*, $C_{11}H_{15}O_4N_2Br$.

The yields of these acids were found to depend on the temperature employed, and the following results were obtained:

At 100°, 65 per cent. $C_{11}H_{14}O_4N_2Br_2$ and 71 per cent. ether extract.
At 130°, 16 „ „ „ „ 70 „ „ „

The best yield of dibromo*iso*pilocarpinic acid was obtained by heating for 6 hours at 100°.

The residual liquid, after extraction with ether, was made alkaline with caustic soda and distilled. The volatile bases obtained were

identified as *ammonia* and *methylamine*, and were present in equal proportions. The soluble hydrochloride gave a platinichloride containing Pt = 41·1 per cent. $(CH_3\cdot NH_2)_2H_2PtCl_6$ requires Pt = 41·3 per cent. The alkaline liquid was next boiled with excess of acid, made alkaline with ammonia, and extracted with chloroform. The chloroform extract yielded a small quantity of dibromo*iso*pilocarpine. The residual liquid was neutralised, evaporated to dryness, the residue extracted with absolute alcohol, and the alcoholic extract saturated with hydrogen chloride. The alcoholic liquid was then distilled, the residue thrown into water, and the aqueous solution extracted several times with ether.

The ethereal liquid was washed with water, dried over calcium chloride, and distilled, when an oil was left of which part distilled at 280—300°, and gave no reaction for nitrogen, but a decided one for bromine. This oil was probably the *ethyl ester* of *bromopilopic acid*. The residual oil was almost solid, and contained both nitrogen and bromine, and probably consisted largely of the *ethyl ester* of *bromopilopinic acid*.

The main products of this reaction are therefore the two bromo*iso*pilocarpinic acids, but a portion of the molecule suffers further oxidation with the splitting off of ammonia and methylamine, and the formation of bromopilopinic and bromopilopic acids, these acids being formed, however, only in small amount.

*Dibromo*iso*pilocarpine*, $C_{11}H_{14}O_2N_2Br_2$.

This substance may be obtained in various ways, but was most economically and conveniently prepared as follows. Forty-six grams of pure *iso*pilocarpine were dissolved in 200 c.c. of glacial acetic acid and to this 72 grams of bromine dissolved in 72 c.c. of glacial acetic acid were gradually added. The precipitate which forms at first was redissolved, and, on standing, crystals of the perbromide separated. One hundred c.c. of water were added, and the mixture allowed to stand for 24 hours. The crystals were then filtered off, washed first with 30 per cent. acetic acid, and then with water, and drained on the filter pump. The crystals of the perbromide were suspended in excess of strong aqueous ammonia, when nitrogen was evolved, and a white, crystalline mass separated. The crystals were filtered off, washed well with cold water, and then recrystallised from hot alcohol until pure. The yield varied from 60 to 70 per cent. of the theoretical.

*Dibromo*iso*pilocarpine perbromide*, $C_{11}H_{14}O_2N_2Br_2,HBr_3$, crystallises from glacial acetic acid in long, yellowish-brown needles which melt at 165° (corr.). The crystals readily lose bromine either on exposure to the air or in solution, and the salt cannot be recrystallised without losing

bromine. A specimen recrystallised once from glacial acetic acid was analysed, with the following result :

0·113 gave 0·152 AgBr. Br = 57·2.

$C_{11}H_{14}O_2N_2Br_2 \cdot HBr_3$ requires Br = 65·9 per cent.

When treated with sodium thiosulphate, the crystals give the calculated yield of dibromo*iso*pilocarpine.

Dibromoisopilocarpine, $C_{11}H_{14}O_2N_2Br_2$, crystallised in well-defined, rectangular, anhydrous prisms which, after frequent recrystallisation from alcohol, melted at 135° (corr.). This melting point was not altered on further recrystallisation. The crystals are almost insoluble in water, alcohol, or ether, but are more soluble in hot alcohol, acetone, or strong acids. A 6 per cent. solution in acetone was optically inactive. On analysis, the following results were obtained :

0·1736 gave 0·2316 CO_2 and 0·0608 H_2O. C = 36·4 ; H = 3·88.

0·2254 „ 15·8 c.c. moist nitrogen at 18° and 766 mm. N = 7·98.

0·2286 „ 0·2326 AgBr. Br = 43·30.

$C_{11}H_{14}O_2N_2Br_2$ requires C = 36·07 ; H = 3·82 ; N = 7·65 ; Br = 43·71 per cent.

This substance is only very feebly basic, it does not react with methyl iodide, and when boiled with excess of dilute acids is recovered unchanged. It dissolves in strong acids, but on dilution the original substance, and not the salt, is precipitated. The perbromide can only be obtained by adding excess of bromine to a solution of the substance in strong hydrobromic acid.

Reduction of Dibromoisopilocarpine.

When dibromo*iso*pilocarpine is reduced either by sodium in amyl alcoholic solution or by zinc and glacial acetic acid, *iso*pilocarpine is formed quantitatively.

(1) *By Sodium in Amyl Alcohol Solution.*—One part of *iso*pilocarpine was dissolved in 20 parts of amyl alcohol (boiling at 135—140°) in a reflux apparatus, and, when the solution was boiling vigorously, one part of sodium was added in two portions. When action had ceased, the alcoholic solution was extracted several times with dilute sulphuric acid, and the acid liquid boiled to remove amyl alcohol and to decompose the sodium salt of *iso*pilocarpine. The acid liquid was then made alkaline with ammonia, extracted several times with chloroform, and the chloroform removed by distillation. The residue obtained was a colourless, thick oil, soluble in water, and alkaline to litmus. It was converted into the nitrate in the usual way, and, after one recrystallisation, this salt melted at 159° (corr.), and when mixed with an equal weight of pure *iso*pilocarpine nitrate melted at the same temperature.

A determination of the specific rotation gave the following result:

$\alpha_D^{18°} = +1°$; $l = 1$ dcm.; $c = 2{\cdot}584$; $[\alpha]_D^{18°} = +38{\cdot}7°$.

For *iso*pilocarpine nitrate $[\alpha]_D = +35{\cdot}7°$.

On analysis:

0·112 gave 0·1986 CO_2 and 0·064 H_2O. C = 48·4; H = 6·3.

$C_{11}H_{16}O_2N_2,HNO_3$ requires C = 48·6; H = 6·3 per cent.

The picrate, prepared in the usual way, melted at 161° (corr.); the platinichloride, which melted at 227°, was analysed, with the following result:

0·0228 gave 0·0054 Pt. Pt = 23·68.

$(C_{11}H_{16}O_2N_2)_2,H_2PtCl_6$ requires Pt = 23·58 per cent.

(2) *By Zinc and Glacial Acetic Acid.*—This is the most convenient method for carrying out the reduction. Dibromo*iso*pilocarpine was dissolved in a convenient quantity of glacial acetic acid, zinc dust added, and the mixture kept at 60—70° for 12—24 hours. The solution was diluted with water, filtered, the filtrate made alkaline with ammonia, and extracted with chloroform. After removing the chloroform by distillation, a residue was obtained which yielded a crystalline nitrate melting at 159° (corr.) and a crystalline picrate melting at 161° (corr.).

The physical constants and analyses just given prove that the base formed by the reduction of dibromo*iso*pilocarpine is identical in all respects with the original base, *iso*pilocarpine.

Oxidation of Dibromoisopilocarpine with Permanganate.

When dibromo*iso*pilocarpine is oxidised with a limited quantity of permanganate, the bromine is eliminated as hydrogen bromide, and, in addition, two acids are formed, *pilopic acid*, $C_7H_{10}O_4$, previously obtained by the oxidation of *iso*pilocarpine with permanganate, and a new acid, *pilopinic acid*, $C_8H_{11}O_4N$, together with methylamine and a small quantity of ammonia. Pilopinic acid is readily oxidised to ammonia and pilopic acid, and hence is only obtained in small quantity, the best yield being 20 per cent. of the theoretical, an equal amount of pilopic acid being formed at the same time. Experiments were made with varying amounts of permanganate, and under different conditions, but the best results were obtained with 3 molecular proportions of permanganate. The formation of pilopinic acid may be expressed by the following equation:

$$C_{11}H_{14}O_2N_2Br_2 + 4O + 2H_2O = C_8H_{11}O_4N + NH_2{\cdot}CH_3 + 2CO_2 + 2HBr.$$

The reaction was carried out as follows. To 36 grams of potassium permanganate dissolved in 600 c.c. of water, 24 grams of finely

powdered dibromo*iso*pilocarpine were added, the mixture well shaken, raised to a temperature of about 80°, and then allowed to stand overnight. The manganese dioxide was filtered off, and the filtrate, which was slightly coloured, decolorised by the addition of a few drops of sulphuric acid, when a little bromine was set free. The liquid was now made alkaline with caustic soda, distilled, and the alkaline distillate collected in hydrochloric acid. This acid solution was evaporated to dryness, when a crystalline residue was obtained which was almost completely soluble in absolute alcohol. The insoluble portion was stable in the air, and was ammonium chloride. The greater portion was soluble in absolute alcohol, and was converted into the platinichloride and analysed, with the following result:

0·092 gave 0·0382 Pt. Pt = 41·5.

$(CH_3 \cdot NH_2)_2, H_2PtCl_6$ requires Pt = 41·3 per cent.

The relative proportion of the bases thus formed is the opposite of that obtained by the oxidation of *iso*pilocarpine when the ammonia forms the larger portion. The alkaline liquid remaining after distillation was neutralised with sulphuric acid, evaporated to dryness, the residue mixed with sand, dried, extracted with hot absolute alcohol, and esterified in a similar manner to the ester obtained from *iso*pilocarpine by oxidation. In this way, 5·3 grams of a very thick oil were obtained. It was distilled under 10 mm. pressure, when about half came over at 180°, leaving a thick oil which distilled at about 250°.

The first fraction was distilled under the ordinary pressure, and after three fractionations the greater part was obtained as an oil which distilled as a pale, straw-coloured, mobile liquid at 290—300°. On analysis, the following results were obtained:

0·1632 gave 0·3487 CO_2 and 0·114 H_2O. C = 58·27; H = 7·76.

$C_9H_{14}O_4$ requires C = 58·07; H = 7·53 per cent.

The ester of lower boiling point was therefore the monoethyl ester of pilopic acid.

The fraction of higher boiling point would not distil under the ordinary pressure, but after refractionation under 10 mm. pressure distilled with difficulty and fairly constant at 262°. On analysis, the following results were obtained:

0·2628 gave 0·5402 CO_2 and 0·1674 H_2O. C = 56·1; H = 7·1.

0·1954 „ 0·4014 CO_2 „ 0·1266 H_2O. C = 56·1; H = 7·2.

0·182 „ 11 c.c. moist nitrogen at 18° and 763 mm. N = 6·86.

$C_{10}H_{15}O_4N$ requires C = 56·3; H = 7·0; N = 6·6 per cent.

This ester is a very pale straw-coloured, thick oil, insoluble in water but soluble in alcohol or ether. It is non-basic, and yields no platinum salt.

Pilopinic Acid, $C_8H_{11}O_4N$.

This acid, obtained by the hydrolysis of its ethyl ester, can be crystallised with considerable difficulty, but is generally obtained as a colourless syrup.

It is best prepared as follows. The pure distilled ester is boiled in a reflux apparatus for several hours with 30 per cent. aqueous sulphuric acid, then transferred to a beaker, boiled with a little animal charcoal, and filtered. The acid solution is saturated with ammonium sulphate and extracted with pure ether, the ether extract washed with water, and then evaporated. On long standing in a vacuous desiccator, crystals are sometimes obtained, but these appear to be mixed with an oily substance, which is sometimes present in sufficient amount to prevent the acid from crystallising. The crystals are drained on a porous tile, and recrystallised from ethereal solution by precipitation with light petroleum. The acid crystallises in pearly plates which melt at 98° and are soapy to the touch. It is soluble in most of the ordinary organic solvents except light petroleum, and this fact renders its separation from the oil, which accompanies it in slight traces, a most difficult matter. The pure crystalline acid was analysed, with the following result:

0·106 gave 0·203 CO_2 and 0·0594 H_2O. C = 52·2; H = 6·2.
$C_8H_{11}O_4N$ requires C = 51·9; H = 5·9 per cent.

The crystals melt readily to an oil, which does not distil undecomposed, even in a vacuum.

Titrated with decinormal alkali, with phenolphthalein as indicator:

0·2138 required, in the cold, 11·7 c.c. for neutralisation, and when boiled with excess of alkali and titrated back with acid, 21·8 c.c.
$C_8H_{11}O_4N$ requires 11·5 c.c. and 23·1 c.c. respectively.

Neither the acid nor the ethyl ester appears to be basic, or forms a salt with platinic chloride.

The acid is lævorotatory, a determination of its specific rotation in dilute alcoholic solution giving the following result:

$$\alpha_D^{16^\circ} = -0{\cdot}4^\circ;\ l = 0{\cdot}5 \text{ dcm.};\ c = 5{\cdot}9;\ [\alpha]_D^{16^\circ} = -13{\cdot}6^\circ.$$

Some of the oily acid which had not been crystallised was converted into the barium salt by boiling with excess of barium carbonate, filtering, evaporating the aqueous solution to a low bulk, and precipitating with absolute alcohol. In this way, the barium salt was obtained as a microcrystalline powder, very soluble in water, but only sparingly so in alcohol. On analysis, the following results were obtained:

0·1948 gave 8·6 c.c. moist nitrogen at 20° and 756 mm. N = 4·9.
0·1064 ,, 0·0466 $BaSO_4$. Ba = 25·8.
$(C_8H_{10}O_4N)_2Ba$ requires N = 5·5 ; Ba = 27·1 per cent.

The results obtained for both nitrogen and barium are low, no doubt owing to slight impurity, but prove conclusively the lactonic monobasic nature of pilopinic acid.

Oxidation of Pilopinic Acid.

The most important point in connection with the study of pilopinic acid was the identification of the nitrogenous product of oxidation. The formation of pilopic acid, together with pilopinic acid, during the oxidation of dibromo*iso*pilocarpine proves almost conclusively that pilopinic acid, on further oxidation, yields pilopic acid, but it was of the utmost importance to determine whether pilopinic acid contained the :NH or the :NCH_3 group present in *iso*pilocarpine.

The whole of the acid and ester at disposal was therefore oxidised with potassium permanganate in excess, the precipitated manganese dioxide removed by filtration, and the filtrate rendered strongly alkaline with caustic soda and distilled. The volatile alkali was converted into the hydrochloride, and yielded a crystalline residue, insoluble in absolute alcohol. The platinichloride prepared from it did not fuse on heating, but gave off white fumes. The only base formed by the oxidation of pilopinic acid is therefore *ammonia*. The oxidation of pilopinic acid may be expressed by the equation :

$$C_8H_{11}O_4N + O + H_2O = C_7H_{10}O_4 + NH_3 + CO_2.$$

Dibromoisopilocarpinic acid, $C_{11}H_{14}O_4N_2Br_2$.

The mode of preparation of this acid has already been described. The crude product was purified by repeated recrystallisation from hot 90 per cent. alcohol until of constant melting point. It crystallises in well-defined, rectangular prisms, which melt with effervescence and decomposition at 235° (corr.). The crystals are fairly soluble in cold alcohol, more so in hot alcohol, but almost insoluble in water or ether. They are anhydrous, but owing to the ease with which they lose bromine when heated they must be dried in a vacuum. On analysis, the following results were obtained :

0·1362 gave 0·1612 CO_2 and 0·0462 H_2O. C = 32·3 ; H = 3·7.
0·1522 ,, 0·1810 CO_2 ,, 0·0502 H_2O. C = 32·4 ; H = 3·7.
0·2284 ,, 0·2718 CO_2 ,, 0·0746 H_2O. C = 32·5 ; H = 3·6.
0·2042 ,, 13·8 c.c. moist nitrogen at 16° and 755 mm. N = 7·6.
0·1538 ,, 0·1442 AgBr. Br = 39·9.
$C_{11}H_{14}O_4N_2Br_2$ requires C = 33·16 ; H = 3·52 ; N = 7·1 ; Br = 40·2 per cent.

The persistently low figures obtained for the carbon in these analyses cannot be explained, although it is possible that the large amount of bromine present may have some effect on the combustion. The acid is dextrorotatory, a determination of its specific rotation in alcoholic solution giving the following result:

$$\alpha_D^{16^\circ} = +1{\cdot}6^\circ;\ l = 1 \text{ dcm.};\ c = 6{\cdot}544;\ [\alpha]_D^{16^\circ} = +24{\cdot}4^\circ.$$

The determination of the basicity of this acid proved unexpectedly to be a most difficult problem. The first attempts were made by titration with cold and hot caustic alkali in the usual manner, and results were obtained indicating a tetrabasic acid. On examining the solution, it was found that the acid had been decomposed and sodium bromide formed.

Attempts to prepare the barium salt were unsuccessful, as even with barium carbonate the acid was decomposed.

The only way by which an approximate titration could be made was as follows:

0·2 gram of acid was dissolved in alcohol and 5·5 c.c. of decinormal sodium carbonate were added; the liquid was found to be distinctly acid to litmus. Five c.c. of alkali were then added, and as the liquid was now distinctly alkaline, it was boiled and rapidly titrated back with decinormal acid; the total amount of decinormal alkali required was thus found to be 7·0 c.c. $C_{11}H_{14}O_4N_2Br_2$, if monobasic, requires 5·0 c.c.

The acid is therefore certainly not dibasic, and, as it acts towards sodium carbonate as a monobasic acid, the excess of alkali used may be due either to slight decomposition of the acid, or to the effect of the lactonic grouping originally present in *iso*pilocarpine.

Attempts to make the silver and ammonium salts were unsuccessful. The basicity was finally determined as follows. About 0·5 gram of acid was dissolved in slight excess of ammonia and then left in a partly exhausted desiccator over sulphuric acid for 18 hours. The solution, which was perfectly neutral to litmus, was precipitated with platinic chloride, the mixture evaporated to a low bulk on the water-bath, alcohol added, and the platinum salt ignited and weighed.

0·4838 acid gave 0·1192 Pt. Pt = 24·63.

$C_{11}H_{14}O_4N_2Br_2$ requires Pt = 24·74 per cent.

Dibromo*iso*pilocarpinic acid is therefore monobasic.

Action of Reducing Agents on Dibromoisopilocarpinic Acid.

(1) *With Sodium in Amyl Alcohol Solution.*—This method having given good results with dibromo*iso*pilocarpine, was first tried. One

gram of acid was dissolved in 20 c.c. of amyl alcohol (boiling point, about 135°) and 2 grams of sodium added in two portions to the boiling solution, which was kept in vigorous ebullition in a reflux apparatus until all the sodium had dissolved.

The alcoholic solution, which was slightly coloured, was extracted by shaking with water, the sodium salt decomposed by boiling with acid, and the acidified aqueous liquid extracted with ether. The ethereal residue, which was very small, crystallised on standing. The crystals melted at 189° (corr.), were insoluble in water, decomposed sodium carbonate solution with effervescence, and were acid to test paper. The quantity obtained was too small to admit of further examination, and attempts made to increase the yield were unsuccessful.

(2) *With Sodium Amalgam in Alcoholic Solution.*—Three grams of the acid were dissolved in alcohol, sodium amalgam was added in considerable excess, and the mixture allowed to stand for several hours. Water was then added, the mixture warmed and filtered. The alkaline liquid was then strongly acidified with sulphuric acid and repeatedly extracted with ether. The ethereal solution was washed with water and distilled to a low bulk, when, on allowing the remainder of the ether to evaporate spontaneously, an oily residue was obtained which after a time crystallised. The crystals were freed from the rancid-smelling oil accompanying them by draining on a porous tile, and were recrystallised from ethereal solution by the addition of light petroleum. After several recrystallisations, they melted at 103° (corr.), and the acid on titration gave the following results:

0·093 gram required for neutralisation in the cold, with phenolphthalein as indicator, 5·7 c.c. decinormal alkali, and after boiling with excess of alkali and titrating back with acid, 10·9 c.c. $C_7H_{10}O_4$ requires 5·9 c.c. and 11·8 c.c. respectively.

The crystalline acid contained no nitrogen, and on analysis afforded the following results:

0·1006 gave 0·1978 CO_2 and 0·0608 H_2O. C = 53·6; H = 6·7.
$C_7H_{10}O_4$ requires C = 53·2; H = 6·3 per cent.

The acid is therefore *pilopic acid*, identical with that obtained from *iso*pilocarpine by oxidation with permanganate. It may be here stated that the acid, $C_7H_{10}O_4$, now termed *pilopic acid*, obtained from *iso*pilocarpine and previously described as an oil, has since been obtained in crystals which melt at 104° (corr.), and may be readily recrystallised from hot benzene solution.

(3) *With Tin and Hydrochloric Acid.*—The reduction carried out by these reagents according to the usual methods afforded a negative result.

(4) *With Zinc and Glacial Acetic Acid.*—The reduction of dibromo-*iso*pilocarpinic acid is best carried out by the following method. The crystalline acid is dissolved in a large quantity (about 20 times its weight) of glacial acetic acid, small quantities of zinc dust are added from time to time, and the mixture kept at 60—70° for about 24 hours. The mixture is then diluted with water, filtered, and the filtrate saturated with hydrogen sulphide. The zinc sulphide is filtered off and the filtrate distilled in a vacuum, with frequent additions of water to remove the greater portion of the acetic and hydrobromic acids. The liquid, after evaporating down to a low bulk, is then left overnight in a vacuous desiccator over caustic potash. The residual varnish is dissolved in hot water, boiled with a little animal charcoal if necessary, and filtered; on cooling, crystals are obtained. These are not crystals of *iso*pilocarpinic acid, as was expected, but of the *lactone of hydroxyisopilocarpinic acid*, $C_{11}H_{14}O_4N_2,H_2O$. The yield is almost quantitative.

Monobromoisopilocarpinic acid, $C_{11}H_{15}O_4N_2Br$.

It has already been stated (p. 504) that by the action of bromine on *iso*pilocarpine in a sealed tube, in addition to dibromo*iso*pilocarpinic acid, a syrupy acid is formed to the extent of about 70 per cent. at 130°. Although, unfortunately, all attempts to obtain this acid in the pure state have failed, yet the identification of its reduction product (by zinc and glacial acetic acid) with that obtained from dibromo-*iso*pilocarpinic acid, together with analyses of partially purified material, renders it possible to state the composition of the amorphous acid with a considerable degree of certainty. The crude ether extract was known to contain, in addition to the main constituent, small quantities of dibromo*iso*pilocarpinic, bromopilopinic, and bromopilopic acids. All attempts to crystallise it having failed, the ether extract was dissolved in strong hydrochloric acid and then precipitated by the addition of water. In this way, it was freed from most of the bromopilopinic and bromopilopic acids. The partially purified acid was then further purified by extraction of the dried residue with anhydrous ether, in which the dibromo*iso*pilocarpinic acid is insoluble. It was thus obtained as a brittle varnish which readily became oily. Analysis of this product showed that it was still impure.

Found, N = 7·0; Br = 31·8.

$C_{11}H_{15}O_4N_2Br$ requires N = 8·7; Br = 25·0 per cent.

The amorphous acid was therefore dissolved in a slight excess of ammonia, the solution allowed to stand overnight over sulphuric acid in a partially exhausted desiccator, and the neutral solution then

precipitated in five fractions with silver nitrate solution. The middle fraction was analysed, with the following results:

0·2128 gave 0·09 AgBr. Ag = 24·3.
0·0954 „ 0·0408 AgBr. Ag = 24·5.
0·1252 „ by Carius' method, 0·0448 AgBr. Br = 15·2.
0·2164 „ 15·2 c.c. moist nitrogen at 17° and 760 mm. N = 8·0.

$C_{11}H_{14}O_4N_2BrAg$ requires Ag = 25·3; Br = 18·7; N = 6·5 per cent.

Although the results of the analyses show that the silver salt was not pure, they point to the correctness of the formula given for this acid, and as the acid on reduction with zinc and glacial acetic acid yields *iso*pilocarpinolactone, $C_{11}H_{14}O_4N_2$, there seems to be conclusive evidence that the main constituent of the ether extract is monobromo-*iso*pilocarpinic acid.

Reduction of Monobromoisopilocarpinic Acid with Zinc and Glacial Acetic Acid.

The reduction of the ether extract of the mother liquors from which the dibromo*iso*pilocarpinic acid had been separated was carried out in precisely the same manner as that of dibromo*iso*pilocarpinic acid (see p. 593). The crystals thus obtained were recrystallised once from water and melted at 83° (corr.), and, when mixed with an equal quantity of the crystals obtained from dibromo*iso*pilocarpinic acid, melted at the same temperature.

The air-dried crystals were analysed, with the following results:

0·1368 gave 0·2568 CO_2 and 0·0774 H_2O. C = 51·2; H = 6·28.

$C_{11}H_{14}O_4N_2,H_2O$ requires C = 51·5; H = 6·25 per cent.

A determination of its specific rotation in alcoholic solution afforded the following result:

$$\alpha_D^{16°} = -1·13°;\ l = 1 \text{ dcm.};\ c = 2·18;\ [\alpha]_D^{16°} = -51·9°.$$

These numbers are identical with those given by the substance obtained from dibromo*iso*pilocarpinic acid by reduction, and conclusively prove the identity of the reduction products of the two acids.

iso*Pilocarpinolactone*, $C_{11}H_{14}O_4N_2,H_2O$.

This substance, obtained as above stated by the reduction of either dibromo- or monobromo-*iso*pilocarpinic acid with zinc and glacial acetic acid, is readily purified by recrystallisation from hot water. When recrystallised until of constant melting point, it was obtained as well-defined, rectangular prisms, which soften at about 80° and melt to a clear liquid at 83° (corr.). The crystals are readily soluble

in hot water, alcohol, acetone, glacial acetic acid, chloroform, or hot benzene, somewhat sparingly so in cold water or benzene and ether and are almost insoluble in light petroleum.

The substance is lævorotatory, and a determination of the specific rotation in alcoholic solution gave the following result:

$$\alpha_D^{16^\circ} = -2{\cdot}1^\circ\ ;\ l = 1 \text{ dcm.}\ ;\ c = 4{\cdot}0464\ ;\ [\alpha]_D^{16^\circ} = -51{\cdot}9^\circ.$$

The crystals contain 1 mol. of water of crystallisation, which is lost even at 60—70°, and the melting point previously given appears to be that of the anhydrous substance, because, after heating the crystals at 100—120° till of constant weight, the residue after powdering melts at 83°. The anhydrous residue was dissolved in dry ether, and on spontaneous evaporation in the air a varnish was left which quickly became crystalline, but the crystals on examination were found to consist of the hydrated lactone. The hydrated lactone was therefore used for the physical constants, analyses, and subsequent experiments, since it is most readily obtained.

The air dried, powdered crystals were analysed with the following results:

0·164, at 100—120°, lost 0·0114 H_2O. $H_2O = 6{\cdot}95$.
0·1838 gave 0·346 CO_2 and 0·105 H_2O. $C = 51{\cdot}34$; $H = 6{\cdot}34$.
0·1018 „ 0·1906 CO_2 „ 0·0564 H_2O. $C = 51{\cdot}1$; $H = 6{\cdot}15$.
0·132 „ 13·3 c.c. moist nitrogen at 18° and 750 mm. $N = 11{\cdot}2$.
$C_{11}H_{14}O_4N_2,H_2O$ requires $H_2O = 7{\cdot}03$; $C = 51{\cdot}5$; $H = 6{\cdot}25$; $N = 11{\cdot}0$ per cent.

The reduction product, therefore, has not the formula expected, namely, $C_{11}H_{16}O_4N_2$, derived from $C_{11}H_{14}O_4N_2Br_2$ by the replacement of 2 atoms of bromine by 2 hydrogen atoms. Further examination of this substance shows that it has somewhat remarkable properties. The aqueous solution is but very feebly acid to litmus, and although the crystals dissolve in sodium carbonate solution, they do so without effervescence.

Attempts were made to titrate the substance with caustic alkali and with sodium carbonate, but when phenolphthalein was used as the indicator it was noted that the change of colour was so gradual that it was not possible to obtain a satisfactory determination, and in this respect the substance differed markedly from pilopinic and pilopic acids, which are readily titrated.

(I) With decinormal alkali:

0·2038, dissolved in alcohol, required 9·8 c.c. of $N/10$ alkali, cold or hot, for neutralisation. $C_{11}H_{14}O_4N_2,H_2O$ (monobasic) would require 8·0 c.c.

(II) With decinormal sodium carbonate:

0·1676, dissolved in hot water, required 3·7 c.c. $N/10$ sodium carbonate to produce a permanent red tint when the liquid was boiled. $C_{11}H_{14}O_4N_2,H_2O$ (monobasic) would require 6·5 c.c.

The lactone was dissolved in hot water and boiled with excess of barium carbonate; after filtration, the substance crystallised out unchanged on cooling.

The *barium* salt of *hydroxyisopilocarpinic acid* was prepared by boiling the lactone with excess of barium hydroxide solution, removing the excess of barium with carbon dioxide, filtering off the barium carbonate, and evaporating the filtrate to a low bulk. The barium salt was readily soluble in water, but separated from the concentrated solution as a microcrystalline powder; it was analysed, with the following result:

0·1986, dried at 130° until of constant weight, lost 0·0204 H_2O and gave 0·0686 $BaSO_4$. $H_2O = 10·3$; $Ba = 20·3$.
$[C_{11}H_{14}(OH)O_4N_2]_2Ba,4H_2O$ requires $H_2O = 10·0$; $Ba = 19·1$ per cent.

The high percentage of barium found is due to the presence of a small amount of barium carbonate formed during evaporation.

The *silver* salt was prepared from the barium salt by adding silver nitrate solution to a concentrated aqueous solution of the barium salt. The amorphous precipitate was well washed with water, collected, dried on a porous tile, and analysed, with the following result:

0·0434 gave 0·0132 Ag. $Ag = 30·4$.
$C_{11}H_{14}(OH)O_4N_2Ag$ requires $Ag = 30·0$ per cent.

This substance is therefore the lactone of hydroxy*iso*pilocarpinic acid, and its formation may be explained as follows.

Only one of the bromine atoms suffers reduction, and the resulting monobromo-acid is decomposed on boiling with dilute acid with the formation of the hydroxy-acid, which loses water and gives the lactone. The reactions of dibromo*iso*pilocarpinic acid previously described indicate that the bromine is readily removed, and render this explanation probable.

*iso*Pilocarpinolactone is also non-basic; it may be recrystallised from hot acidified water, and when heated with methyl iodide in alcoholic solution is recovered unchanged. Even when heated with excess of methyl iodide in alcoholic solution in a sealed tube at 100° for 2 hours, no reaction took place, and the lactone was recovered unchanged. This non-basic character of *iso*pilocarpinolactone has, as will be shown later, a most important bearing on the constitution of the alkaloid.

Dibromopilocarpine, $C_{11}H_{14}O_2N_2Br_2$.

Chastaing (*Compt. rend.*, 1883, 97, 1435) first described an amorphous product produced by the bromination of pilocarpine, but Pinner and Kohlhammer (*loc. cit.*) have prepared the crystalline dibromopilocarpine, and have described it somewhat briefly. According to these authors, the properties of dibromopilocarpine differ in some important respects from those of the isomeric dibromo*iso*pilocarpine described in another part of this paper. It was therefore considered necessary to prepare this substance and examine it in a more complete manner. The dibromopilocarpine was prepared according to the method given by these authors, and a yield of 71 per cent. of the theoretical obtained. This agrees fairly well with the yield of the isomeric dibromo*iso*pilocarpine (p. 585), but in this case the mother liquors were not further examined.

Dibromopilocarpine, prepared from pure pilocarpine nitrate (m. p. 176°), as first obtained, melted at 84°, and after frequent recrystallisation from 50 per cent. alcohol, separated in fine, colourless prisms which melted sharply at 95° (corr.). This melting point was not altered on further recrystallisation of the compound, so that the temperature given by Pinner and Kohlhammer, namely, 79°, is too low. Further, it was found that the substance could be readily recrystallised from hot 50 per cent. alcohol, whilst the above authors state that the crystals separate after long standing.

The crystals were air-dried and analysed, with the following results:

0·1436 gave 0·1904 CO_2 and 0·0498 H_2O. C = 36·2; H = 3·85.
0·1676 „ 0·2236 CO_2 „ 0·0578 H_2O. C = 36·4; H = 3·83.
0·1734 „ 0·1776 AgBr. Br = 43·59.
$C_{11}H_{14}O_2N_2Br_2$ requires C = 36·07; H = 3·82; Br = 43·71 per cent.

Dibromopilocarpine is dextrotatory like the parent base pilocarpine, and a determination of its specific rotation in alcoholic solution gave the following result:

$$\alpha_D^{15°} = +1·5°;\ l = 1 \text{ dcm.};\ c = 3·444;\ [\alpha]_D^{15°} = +43·6°.$$

Like its isomeride dibromo*iso*pilocarpine, dibromopilocarpine is very feebly basic, although Pinner and Kohlhammer state that its salts are all readily soluble. This important point was proved by the following experiments. Dibromopilocarpine was dissolved in excess of hot dilute sulphuric acid; on cooling, crystals separated which were proved, by the melting point and absence of any reaction with barium chloride, to be unchanged dibromopilocarpine. Further, the substance was recovered unchanged after boiling with methyl iodide. The two isomeric bromo-derivatives have, therefore, similar properties.

Reduction of Dibromopilocarpine.

This was carried out with zinc and glacial acetic acid, as described for dibromo*iso*pilocarpine, the use of sodium and amyl alcohol being inadmissible in this case, since pilocarpine is converted into *iso*pilocarpine by this reagent.

The dibromopilocarpine gave a quantitative yield of a basic, colourless oil, soluble in water, which, with nitric acid, yielded a crystalline nitrate melting at 176°. The salt was once recrystallised from hot alcohol, and then melted at 177° (corr.).

A determination of its specific rotation in aqueous solution gave the following result:

$$a_D^{18°} = +1{\cdot}8°;\ l = 1 \text{ dcm.};\ c = 2{\cdot}184;\ [a]_D^{18°} = +82{\cdot}4°.$$

Pilocarpine nitrate melts at 177—178° (corr.) and has $[a]_D = +82{\cdot}9°$. By the reduction of dibromopilocarpine there is formed quantitatively *pilocarpine*, identical in all respects with the parent base.

Bromocarpinic acid, $C_{10}H_{15}O_4N_2Br$.

This acid is stated by Pinner and Kohlhammer to be formed, together with another acid not yet examined, by the action of bromine on pilocarpine at 100° in a sealed tube, and to be a dibasic acid. It possesses, therefore, especial interest for two reasons, first, because it proves that the isomerism of pilocarpine and *iso*pilocarpine is structural and not stereoisomeric, since *iso*pilocarpine, by a similar reaction, yields dibromo*iso*pilocarpinic and monobromo*iso*pilocarpinic acids, and, secondly, because it completes the series of acids capable of formation between the parent base and pilopic acid by successive elimination of the three carbon atoms and the groups :NH and :NCH_3.

In view of the importance, therefore, of this compound, it was thought advisable to repeat the experiments.

Two experiments were conducted under the conditions detailed by Pinner and Kohlhammer, but in neither case could any crystalline product be isolated. This was the more remarkable as parallel experiments were proceeding at the same time on *iso*pilocarpine, and the crystalline dibromo*iso*pilocarpinic acid was readily obtained. The acid liquors from the bromination of pilocarpine were therefore extracted with ether, the ethereal extract distilled, and the residue reduced with zinc and glacial acetic acid in the usual manner. An oily substance was thus obtained which was insoluble in cold water, but fairly soluble in boiling water, and sparingly so in ether. Attempts to crystallise it from hot water and other solvents having failed, the oil was boiled twice with water, separated, and then taken up with ether. The

ethereal solution was washed many times with water to remove all acids soluble in water, and, on removing the ether by distillation, a residue was left which could not be crystallised. It was therefore dried in a vacuum over sulphuric acid, and titrated with decinormal sodium carbonate and with decinormal caustic alkali, with the following results:

1. 0·4256 required 17·8 c.c. *N*/10 sodium carbonate for neutralisation. $C_{10}H_{16}O_4N_2$ requires 37·3 c.c.; $C_{11}H_{16}O_4N_2$ requires 17·7 c.c.

2. 0·1856 required 8·0 c.c. *N*/10 sodium hydroxide cold and 10·4 c.c. hot. $C_{10}H_{16}O_4N_2$ requires 16·3 c.c.; $C_{11}H_{16}O_4N_2$ requires 7·7 c.c.

The end reaction in the second titration was not sharp, particularly when the solution was hot. The amorphous residue, which contained no bromine, was boiled with excess of barium carbonate, and the barium salt separated in the usual way by precipitation with alcohol. On analysis, the following result was obtained:

0·1764 gave 0·0664 $BaSO_4$. Ba = 22·14.

$C_{10}H_{14}O_4N_2Ba$ requires Ba = 37·7 per cent.

$(C_{11}H_{15}O_4N_2)_2Ba$ „ Ba = 22·3 „

The results of these experiments prove conclusively that in this case bromocarpinic acid is not formed, and they indicate with a considerable degree of probability that the action of bromine on pilocarpine under these conditions is analogous to the action on *iso*pilocarpine, namely, the formation of mono- or dibromo-pilocarpinic acid, and subsequent reduction of these acids to pilocarpinic acid. This view is supported by the experimental data, by analogy with *iso*pilocarpine, and by the fact that by similar reactions with *iso*pilocarpine a homogeneous product is formed, although, fortunately, in this case it was crystalline. It is hardly possible that such an amount of impurity could be present, if the acid be carpinic acid, as to account for the analytical results, and to produce the coincidence of these results with those required for pilocarpinic acid. It is possible that the acid formed under the conditions of these experiments is identical with that observed but not examined by Pinner and Kohlhammer.

Experiments on the Oxidation of iso*Pilocarpine.*

Experiments were made with various oxidising agents under varying conditions to see if any intermediate products of oxidation could be isolated. Although these experiments gave a negative result, they are placed on record, as they have an important bearing on the constitution of the alkaloid.

(1) *With Alkaline Permanganate.*—When *iso*pilocarpine is dissolved in sodium carbonate solution, and titrated with potassium perman-

ganate at 0°, oxidation takes place very quickly, the colour of the first few drops being discharged instantly and the reaction then proceeds quickly, but not instantaneously, each atomic proportion of oxygen requiring about 5 minutes for complete absorption. In this way, 5 atomic proportions of oxygen are quickly absorbed, but after that the reaction appears to proceed more slowly. To *iso*pilocarpine dissolved in alkali, potassium permanganate representing 5 atomic proportions of oxygen was added. The colour was quickly discharged, but on working up the volatile bases obtained it was found that the ammonia and methylamine had been produced in about equal proportion, so that it was not possible to prepare the pilopinic acid in this manner.

(2) *With Acid Permanganate.*—*iso*Pilocarpine in aqueous sulphuric acid solution was titrated with normal potassium permanganate solution at 15°, but oxidation proceeded very slowly indeed, the average time taken for the complete absorption of an atomic proportion of oxygen being 2 hours. No point was reached at which the action seemed to cease, and the results indicated that the oxidation was proceeding to some simple final product.

(3) *With Potassium Dichromate.*—*iso*Pilocarpine nitrate was treated with an equal weight of potassium dichromate in sulphuric acid solution for 12 days at 15°, and then for several hours at 80°, but no reaction took place, and the *iso*pilocarpine was recovered unchanged.

(4) *With Chromic Acid.*—When treated with an equal weight of chromic acid in aqueous solution for several days at the ordinary temperature, *iso*pilocarpine is recovered unchanged.

Pinner and Kohlhammer (*Ber.*, 1900, **33**, 2363) have stated that by the action of chromic acid on pilocarpine in sulphuric acid solution at the temperature of a water-bath, pilocarpoic acid, $C_{11}H_{16}O_5N_2$, is formed, and this acid with barium hydroxide yields a barium salt, $C_{11}H_{14}O_5N_2Ba$, which was only obtained in the amorphous condition. Their analyses, however, do not agree very well for the above formula, and a homogeneous product was hardly to be expected from such a reaction. Similar experiments have been carried out on *iso*pilocarpine with a negative result. No crystalline acid could be obtained from the products of the reaction, and the barium salts formed were of such an uninviting character that it was not considered worth while to analyse them. When the acid was regenerated from the barium salt, a rancid odour, recalling that of butyric acid, was noticed, so it was probable that the oxidation had been more complex than indicated by the authors above mentioned. The stability of both pilocarpine and *iso*pilocarpine towards strong nitric acid has already been noticed.

Action of Various Reagents on iso*Pilocarpine.*

The behaviour of *iso*pilocarpine towards bromine and alkaline permanganate suggested the possibility of the existence of a double bond in the part of the molecule other than that giving rise to pilopic acid, and as this point was of considerable importance, experiments were made to settle it. The reduction of dibromo*iso*pilocarpine to *iso*pilocarpine by various reducing agents had proved conclusively that bromine acts as a substituting and not as an additive agent, and experiments made by mixing chloroform solutions of *iso*pilocarpine and bromine showed that under no conditions was a dibromo-additive compound formed. Attempts were therefore made to reduce *iso*pilocarpine, but without success. Even when heated with four times its weight of fuming hydriodic acid at 127° in a reflux apparatus for 4 hours, the base was recovered unchanged. Sodium in boiling amyl alcohol or zinc and glacial acetic acid, even when acting on the base in a nascent condition, have been shown to be without action on *iso*pilocarpine (p. 586). Finally, the base was dissolved in glacial acetic acid saturated with hydrogen bromide, and allowed to stand many days, but no reaction took place other than the formation of *iso*pilocarpine hydrobromide. These experiments show conclusively that *iso*pilocarpine contains no ordinary double bond.

Discussion of Results.

The full discussion of the results recorded in this paper is reserved for a future communication, but a brief allusion may be made to one important point which arises out of the data here recorded. Two of the most important characters of *iso*pilocarpine which are not easy to explain are the non-basic nature of the methylamine residue and the peculiar behaviour of the carboxyl residue, which approximates most to a lactone, although the salt formed with barium hydroxide is decomposed by carbonic acid.

The results recorded in this paper give, however, a clue to the reason for this behaviour.

When an acidic group, for example, bromine or carboxyl, is introduced into *iso*pilocarpine, the ammonia residue loses its basicity, or at least to a very great extent. This happens in the case of dibromo*iso*pilocarpine, where the molecular structure remains unchanged, and also in *iso*pilocarpinolactone, where the molecular structure is probably altered. This "intramolecular neutralisation" of a basic nitrogen atom by carboxyl or bromine is unusual, as in many substances, for example, ecgonine [or] the pyridinecarboxylic acids, which contain an

acidic and basic element or groups, the dual property of acting as a base and an acid remains intact.

The fact is, however, that the introduction of these acidic groups into the molecule of *iso*pilocarpine does destroy (or nearly so) the basic character. This affords an explanation of the fact that the methylamine residue in *iso*pilocarpine is non-basic, for there already exists in the alkaloid a carboxyl residue, and these two groups may neutralise each other within the molecule and therefore leave a substance in which only the other nitrogen atom exerts a basic action. It is also conceivable that this intramolecular neutralisation may so modify the lactonic character as to cause the alkaloid to behave in the peculiar manner already indicated. This appears to be a much more probable explanation than the alternative one, which is that the nitrogen of the methylamine residue is pentad, and hence cannot react with methyl iodide, &c.

The further investigation of this subject is proceeding, particularly in reference to the constitution of pilopic acid, and it is hoped to communicate the results to the Society at a later date.

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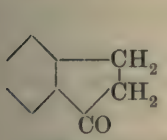
LXIII.—*Pheno-α-ketoheptamethylene and its Derivatives.*

By FREDERIC STANLEY KIPPING, Ph.D., D.Sc., F.R.S., and ALBERT E. HUNTER.

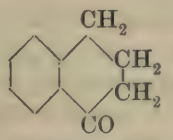
THE intramolecular condensation of phenylpropionic chloride in presence of anhydrous aluminium chloride results, as previously shown (Kipping, Trans., 1894, **65**, 680) in the formation of the cycloid ketone, α-hydrindone, and by an exactly analogous reaction, phenylbutyric chloride is converted into α-ketotetrahydronaphthalene (Kipping and Hill, Trans., 1899, **75**, 144).

This method of obtaining cycloid ketones has now been applied to the next higher homologue of this series of acid chlorides, and it is shown in this paper that phenylvaleric chloride, $C_6H_5 \cdot [CH_2]_4 \cdot COCl$, can be converted into a ketone which has been named pheno-α-ketoheptamethylene.

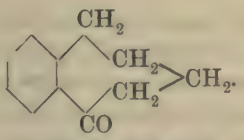
The relationship between the three closed chain compounds which have thus far been prepared with the aid of this reaction is shown by the following formulæ:



α-Hydrindone.

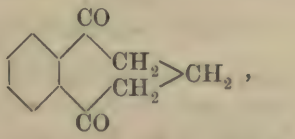


α-Ketotetrahydronaphthalene.



Pheno-α-ketoheptamethylene.

Pheno-α-ketoheptamethylene, as will be seen from its formula, contains a closed chain of *seven* carbon atoms condensed with a benzene nucleus, and when briefly described about nine months ago by Kipping and Hall (Proc., 1899, **15**, 173),* it was the first compound of this type which had been prepared; very shortly afterwards, however, Dieckmann gave a short account (*Ber.*, 1899, **32**, 2247) of a closely related compound, namely, pheno-1 : 5-diketoheptamethylene,



which he had obtained by condensing ethyl phthalate with ethyl-glutarate,

$$C_6H_4\begin{matrix}CO\cdot OEt\\CO\cdot OEt\end{matrix} + CH_2\begin{matrix}CH_2\cdot CO_2Et\\CH_2\cdot CO_2Et\end{matrix} =$$

$$C_6H_4\begin{matrix}CO\cdot CH(CO_2Et)\\CO\cdot CH(CO_2Et)\end{matrix}>CH_2 + 2C_2H_5\cdot OH,$$

and then boiling the product with dilute sulphuric acid, which first hydrolyses the ester, and then eliminates the two carboxyl groups; it seems probable, therefore, that compounds of this type will soon be familiar to chemists.

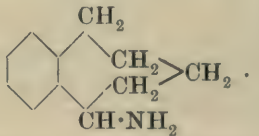
Pheno-α-ketoheptamethylene is a colourless oil and has only a slight smell at the ordinary temperature, but when warmed it gives off a vapour having a strong odour of peppermint. The property of affecting the olfactory organs in the same way as does menthol seems to depend partly, in the case of these aromatic-fatty cycloid ketones, on the number of methylene groups in the reduced ring; hydrindone, for example, has an odour recalling that of jasmine, but the vapour of ketotetrahydronaphthalene has a distinct, although not a very strong, smell of peppermint, and that of the next higher homologue, as just stated, is very marked.

The constitution of pheno-α-ketoheptamethylene is established by its method of formation, which is almost certainly analogous to that of

* Miss Hall was unable to continue this investigation; the authors desire to thank her for the work which she did in connection with it.

α-ketotetrahydronaphthalene (*loc. cit.*); that it is a ketone is shown by the formation of an oxime and a semicarbazone, which are described later; that it contains the heptamethylene ring condensed with the benzene nucleus in the *ortho*-position is proved by the fact that on oxidation with nitric acid it yields, among other products, *o*-phthalic acid.

Just as the oxime of α-ketotetrahydronaphthalene gives on reduction α-aminotetrahydronaphthalene, so the oxime of pheno-α-ketoheptamethylene is reduced to an α-amino-derivative of the following constitution:



Pheno-α-aminoheptamethylene.

This base is a colourless liquid, having the normal properties of a primary amine, and with acids it forms well-defined salts; when its hydrochloride is submitted to dry distillation, it is decomposed, giving a non-basic product which is, in all probability, an unsaturated hydrocarbon, formed from the base by a reaction analogous to that by which indene is produced from hydrindamine hydrochloride (Kipping and Hall, Trans., 1900, 77, 469); this product is being investigated.

Preparation of Phenylvaleric Acid.

The preparation of phenylvaleric acid in considerable quantity for the purpose of this investigation proved to be a rather troublesome process, and we have not been able to improve on the method originally employed by von Baeyer and Jackson (*Ber.*, 1880, 13, 122).

The first step consists in the synthesis of cinnamylidenemalonic acid, a compound which is easily obtained in large quantities by the condensation of cinnamaldehyde with malonic acid in the presence of glacial acetic acid or acetic anhydride,

$$C_6H_5\cdot CH{:}CH\cdot CHO + CH_2(CO_2H)_2 = C_6H_5\cdot CH{:}CH\cdot CH{:}C(CO_2H)_2 + H_2O;$$

the reduction of this acid is also readily accomplished in alkaline solution with the aid of sodium amalgam; and on subsequently acidifying the ice-cold solution, hydrocinnamylidenemalonic acid,

$$C_6H_5\cdot CH_2\cdot CH{:}CH\cdot CH(CO_2H)_2,$$

is precipitated in colourless crystals (compare Thiele and Meisenheimer, *Annalen*, 1899, 306, 260).

This substance, when boiled with water, decomposes into hydro-

cinnamylideneacetic acid, $C_6H_5 \cdot CH_2 \cdot CH{:}CH \cdot CH_2 \cdot CO_2H$, and carbon dioxide.

So far, the yields are almost quantitative, but the reduction of the hydrocinnamylideneacetic acid to phenylvaleric acid has to be done with an aqueous or acetic acid solution of hydrogen iodide in sealed tubes, all other reducing agents which have been tried having failed to bring about the desired change; the contents of the tubes are generally rather dark in colour, and the acid must be purified by recrystallisation from water, in which it is sparingly soluble, and then from light petroleum; it is thus obtained in almost colourless, rhomboidal crystals melting at 59°.

Phenylvaleric chloride was obtained by heating the acid with rather more than the calculated quantity of phosphorus pentachloride in a Wurtz flask, and then heating on the water-bath under greatly reduced pressure until all the phosphorus oxychloride had distilled over; it is a colourless, mobile liquid, which does not fume in the air, and has only a very faint odour.

The Action of Aluminium Chloride on Phenylvaleric Chloride.

The conversion of phenylvaleric chloride into pheno-α-ketoheptamethylene does not take place as readily as that of phenylpropionic chloride into hydrindone, and a rather higher temperature seems to be required to bring about the change; the reaction is also very incomplete, so that the actual yield of ketone is small.

On the other hand, by using the right proportion of aluminium chloride, the formation of tarry products can be almost entirely prevented, and a large proportion of the unchanged acid can be recovered; allowing for this, the yield is by no means unsatisfactory, and amounts on the average to 30 or 40 per cent. of the calculated amount. The following conditions have been found to give the best results: Phenylvaleric chloride (5 parts) is dissolved in about six times its volume of light petroleum (b. p. 60—80°); finely powdered aluminium chloride (6 parts) is added slowly, and the mixture is rapidly heated on a bath of boiling water; as soon as the temperature rises to about 70°, the evolution of hydrogen chloride sets in, and a fairly vigorous reaction continues so long as the mixture is heated, and almost constantly shaken; after about 30 minutes, by which time the contents of the flask have separated into two layers, the liberation of hydrogen chloride shows marked signs of abating, and the flask is quickly cooled.

After cautiously adding water, the petroleum is separated by distilling in steam, and the process is continued so long as ketone comes over; the latter is isolated by extracting the distillate with a little

light petroleum or ether, washing with dilute sodium carbonate solution, and then evaporating the dried extract.

The clear aqueous solution left after steaming contains a little regenerated phenylvaleric acid, which can be separated from the small quantity of resinous matter by filtration, and further quantities of the acid may be obtained by repeatedly extracting this bye-product with water.

Pheno-α-ketoheptamethylene, $C_6H_5<\begin{matrix}CH_2\cdot CH_2\\CO-CH_2\end{matrix}>CH_2$.

The crude phenoketone, obtained by evaporating its solution in ether or light petroleum, is an almost colourless, moderately mobile liquid, which seems to be practically free from any appreciable quantity of impurity; if necessary, it can be purified by distillation under reduced pressure, or by converting it into the crystalline semicarbazone and decomposing the latter with dilute sulphuric acid (see below).

When obtained by the second method, it is a colourless oil, specifically heavier than water, but it turns yellowish on exposure to the air. It does not solidify when cooled to 0°, or when kept for a long time at the ordinary temperature; since hydrindone melts at 44°, it would seem that the melting points of these cycloid ketones become lower as the number of carbon atoms in the reduced chain increases.

It is practically insoluble in water, but is miscible with all ordinary organic solvents; it volatilises slowly in steam, and boils at about 270° under atmospheric pressure, apparently decomposing slightly; when boiled with water, the escaping vapour has a strong odour of peppermint.

It interacts readily with phenylhydrazine, and with *p*-bromophenylhydrazine when it is warmed gently with either of these reagents, but the products do not crystallise at all readily, and are quite unsuitable for purposes of identification or isolation; they also undergo decomposition, and turn reddish-brown on exposure to the air.

The oxime and the semicarbazone, on the other hand, crystallise very readily, and are easily purified.

Pheno-α-ketoheptamethylene is readily attacked by bromine and by bromine water, giving crystalline products which, however, have not yet been examined; its behaviour towards oxidising agents is described later.

Pheno-α-ketoheptamethylene Semicarbazone, $C_{11}H_{12}{:}N\cdot NH\cdot CO\cdot NH_2$.—This compound is gradually deposited in colourless crystals when a solution of the crude ketone in dilute alcohol is warmed on the water-bath with sodium acetate and semicarbazide hydrochloride, and after some hours the reaction is complete; for analysis, the product was recrystallised from boiling alcohol and dried at 100°.

0·1506 gave 0·3669 CO_2 and 0·0975 H_2O. C = 66·4 ; H = 7·2.
0·1434 „ 0·3484 CO_2 „ 0·0896 H_2O. C = 66·3 ; H = 6·9.
$C_{12}H_{15}ON_3$ requires C = 66·4 ; H = 6·9 per cent.

Pheno-α-ketoheptamethylene semicarbazone separates from alcohol in highly lustrous, silky plates, melting at 206—207° if heated slowly from 200°, decomposing and giving off bubbles of ammonia ; if heated rapidly, the substance may not melt until 214—215° (219—220° corr.).

It is readily soluble in boiling chloroform, methyl or ethyl alcohol, ethyl acetate, acetone, or acetic acid, but only sparingly so in hot light petroleum, and is practically insoluble in water. It is decomposed by warm dilute hydrochloric or sulphuric acid, the ketone being regenerated ; this fact, and the readiness with which the semicarbazone crystallises, make the isolation and identification of the ketone a simple matter, even when only a very small quantity is available.

Although many cycloid ketones afford isomeric semicarbazones, this does not seem to be the case with pheno-α-ketoheptamethylene ; its semicarbazone was fractionally crystallised from alcohol, and thus separated into five fractions, but they all melted at the same temperature.

Pheno-α-ketoheptamethylene Oxime, $C_{11}H_{12}{:}N{\cdot}OH$, is obtained when the ketone, regenerated from the semicarbazone, is heated in alcoholic solution with slight excess of hydroxylamine hydrochloride and potash and the mixture allowed to stand for some time. On adding a little water, the separation of a crystalline compound soon commences, and the last portions may be obtained by gently evaporating the solution on the water-bath, and subsequently acidifying it. The oxime is readily purified by recrystallisation from dilute methyl alcohol or light petroleum, from which it is deposited in long needles having a silky lustre, and melting at 108—109°.

Pheno-α-ketoheptamethylene oxime is very readily soluble in methyl or ethyl alcohol, acetone, acetic acid, or ether, but only moderately so in boiling light petroleum ; it also dissolves freely in cold potash solution, but is only sparingly soluble in water or dilute acids.

Oxidation of Pheno-α-ketoheptamethylene.

Pheno-α-ketoheptamethylene is only very slowly oxidised by potassium permanganate in presence of sodium carbonate, but on warming, oxidation proceeds fairly rapidly. It is readily attacked by hot dilute nitric acid, but apparently the reaction is not a simple one, as in the case of most of the fatty cycloid ketones, and various products are generated.

In order to try and obtain some evidence in favour of the view

that the ketone contains a closed chain of seven carbon atoms, that is, that it has been produced from the acid chloride by condensation in the ortho-position, as in the cases previously examined, some of the pure substance was treated with dilute (about 5 per cent.) nitric acid; on heating, brown fumes were evolved, and after boiling for about half an hour most of the ketone seemed to be changed.

On cooling, a brownish, flaky mass separated at the surface, and at the bottom of the liquid there was a considerable quantity of oil. These two products were collected separately, the nitric acid solution was concentrated, filtered when cold to remove oily matter, and then evaporated to dryness.

The almost colourless crystalline residue, when purified by recrystallisation from water, melted at about 185°, and was readily soluble with effervescence in dilute sodium carbonate solution; when gently heated, it gave a sublimate which consisted of long needles melting sharply at 127—128°, and did not dissolve immediately in cold dilute sodium carbonate solution.

These are properties of phthalic acid and its anhydride, and the fact that this acid is formed on oxidation is confirmatory evidence that the ketone has the constitution assigned to it. Phthalic acid, however, is not the principal product resulting from the above treatment, as a considerable quantity of the ketone is converted into the oily product mentioned above; this oil is soluble in cold dilute sodium carbonate solution, is reprecipitated on the addition of acids, and is apparently unchanged on prolonged heating with nitric acid; as it could not be made to crystallise, it does not seem probable that it could be *o*-carboxyphenylbutyric acid, $CO_2H \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, which melts at 138° (Roser, *Ber.*, 1885, **18**, 3118), although the formation of this acid under the above circumstances was to be expected.

The second bye-product, namely, the brownish solid referred to above, was easily obtained in a pure state by recrystallising it several times from methyl alcohol, from which it separated in concentrically-grouped prisms melting at 159—160°; this compound was practically insoluble in water or boiling dilute sodium carbonate solution, and it was not changed appreciably by prolonged treatment with hot moderately concentrated nitric acid, in which it was only very sparingly soluble.

The further investigation of these bye-products did not seem to be of sufficient importance to render desirable the sacrifice of a large quantity of the ketone.

Pheno-a-aminoheptamethylene, $C_6H_4<^{CH_2\cdot CH_2\cdot CH_2}_{CH(NH_2)\cdot CH_2}>$.

This compound is easily obtained by the reduction of the oxime in alcoholic solution with sodium amalgam, keeping the solution slightly acid with acetic acid. After several times the calculated quantity of amalgam had been used, the solution was submitted to distillation in a current of steam, and, as little or no unchanged oxime passed over, the contents of the flask were cooled and made strongly alkaline with potash, and the liquid again distilled in steam. A strongly basic, colourless oil then passed over, and the distillate was collected in dilute hydrochloric acid, the solution being afterwards evaporated to dryness on the water-bath, when a considerable quantity of a white, crystalline salt was obtained.

The amount of amine produced seemed to be practically theoretical, the reduction being rapidly accomplished without any difficulty.

The base is only sparingly soluble in water, but dissolves readily in the ordinary organic solvents; it rapidly absorbs carbon dioxide from the air, giving a crystalline product.

The *hydrochloride* is obtained by crystallisation from hot water in rosette-like aggregations of short, microscopic needles; it is readily soluble in methyl or ethyl alcohol, or in hot water, moderately so in cold water, but only sparingly so in chloroform, acetone, or light petroleum. It did not melt on being heated up to 250°.

The *platinichloride*, $(C_{11}H_{15}N)_2,H_2PtCl_6$, was obtained as a yellow precipitate on mixing strong aqueous solutions of the hydrochloride and platinic chloride. It crystallises from hot water in felted masses of needles of a light orange colour, having no definite melting point, and is very readily soluble in methyl or ethyl alcohol.

The air-dried salt, on being heated at 100° during several hours, did not diminish in weight. On analysis:

0·2998 gave 0·0796 Pt. Pt = 26·54.

$(C_{11}H_{15}N)_2,H_2PtCl_6$ requires Pt = 26·66 per cent.

On ignition, the compound gave off vapours having an odour like that of naphthalene or indene, a behaviour similar to that of the hydrochloride.

The *sulphate*, prepared by neutralising the base with dilute sulphuric acid, is very suitable for the purification of the amine, as it is more sparingly soluble in water than the hydrochloride, and crystallises in thin, transparent plates. It dissolves easily in hot water, but only sparingly in cold water or alcohol; it melts and decomposes at about 227—229°.

The *oxalate*, made in a similar manner, is deposited from water in irregular prisms, which are moderately soluble in water or alcohol, but only slightly so in ethyl acetate.

The *picrate* is deposited in yellow needles when a solution of the oxalate is mixed with an aqueous solution of picric acid; it crystallises from hot water in felted masses of pale yellow needles, which decompose on being heated; it is very soluble in hot water, but only sparingly so in cold water.

The *benzoyl* derivative, obtained by the Schotten-Baumann reaction and purified by crystallisation from dilute alcohol, forms felted masses of needles melting at 171—172°. By means of this compound small quantities of the amine may be identified, as it is easily purified, and is practically insoluble in water.

The authors desire to thank the Government Grant Committee of the Royal Society for a grant in aid of this research.

UNIVERSITY COLLEGE,
NOTTINGHAM.

LXIV.—*The Chemical Action of Bacillus coli communis and Similar Organisms on Carbohydrates and Allied Compounds.*

By ARTHUR HARDEN.

THE following experiments were undertaken with the object of examining quantitatively the mode of action of the organisms of the Colon group as fermentative agents, in the hope of finding some characteristics which might serve as a means of classification or discrimination. The organisms of this group can scarcely be distinguished microscopically, but are found to vary in their action on various sugars and proteid compounds. The *Bacillus coli communis*, at one end of the series, has the following characteristic properties:

(*a*) It decomposes glucose with production of (1) acid and (2) gas.

(*b*) It curdles milk.

(*c*) It produces indole from peptone.

The *Bacillus typhosus*, which may be taken as the other extreme of the series, does not possess properties *b* and *c*, and decomposes glucose with production of acid, but not of gas. Intermediate in the series are a number of organisms, which possess one or more, but not all, of the properties of *B. coli communis* or *B. typhosus*.

The action of *B. coli communis* and of *B. typhosus* on glucose has

therefore been examined, as far as possible quantitatively, in order to obtain a standard with which that of the other organisms might be compared, and this comparison has been effected for three different organisms. The action of *B. coli communis* on *d*-fructose and mannitol has also been examined in detail.

The products of the fermentation of glucose by these organisms comprise lactic acid, succinic acid, acetic acid, ethyl alcohol, formic acid, carbon dioxide, and hydrogen, all of which have been quantitatively estimated.

The *Bacillus coli communis*, and similar organisms, grow well and bring about a vigorous fermentation of glucose in a large number of different nutrient media. Thus they are able to derive their nitrogen from inorganic salts of ammonium and of methylammonium, from simple amino-acids, such as asparaginic acid, from Witte's peptone, and from beef broth. Since the products of the fermentation are acid in character, it is necessary to carry out the process in presence of chalk in order to neutralise the acid as it is produced. When ammonium salts are employed, it is therefore necessary to sterilise the solution of the sugar containing the chalk separately from the solution of the ammonium salt, in order to avoid the loss of ammonia which would otherwise ensue. The solution of the ammonium salt must therefore be sterilised in a flask arranged like an ordinary wash-bottle, so that the liquid, before inoculation, can be driven over into the sugar solution by a current of sterile air. When a culture in such a medium is incubated at 37°, it is found that the fermentation of the sugar commences very slowly, a delay of as much as five days occurring in some cases, although after this initial period the action is as vigorous as in the presence of peptone alone. This delay is no doubt due to the alkalinity of the solution, caused by the liberation of ammonia by the action of the chalk on the ammonium salt, which renders the development of the organism extremely slow until sufficient acid has been produced to render the medium capable of promoting growth at the normal rate.

This is shown by the figures on p. 612, from which it is seen that although in the end nearly the whole of the sugar is decomposed, the evolution of gas commences much more slowly when ammonium or methylammonium salts are present than when peptone alone is employed.

As the action of the free ammonia might seriously affect the mode of growth and action of the organism, this form of nitrogenous nourishment is not well adapted for comparative experiments. Asparaginic acid is equally unsuitable, but from a different and very interesting cause. As will be shown, it undergoes reduction under these circumstances to ammonium succinate, a large proportion of the

Nitrogenous medium.	Gas evolved at the end of days						Total gas evolved c.c.	Total sugar decomposed. Grams.
	1.	2.	3.	4.	5.	6.		
Peptone	500	1560	2270	3400	3500	3600	3700	20
Ammonium sulphate...	—	—	—	100	690	2630	4980	20
Methylammonium sulphate...	—	60	960	2210	—	3430	3650	17·87

hydrogen which is evolved when other media are employed being thus absorbed. Moreover, the large amount of succinic acid produced renders the analytical separation of the products more difficult.

It is also difficult to obtain satisfactory analytical results with media containing beef broth or extract of meat, because this contains small quantities of sugar and *d*-lactic acid, and the products derived from these cannot easily be separated from those derived from the sugar undergoing examination. The sum of the products obtained in this medium is invariably greater than the weight of the sugar taken.

The most satisfactory medium, from this point of view, was found to be peptone water, prepared by boiling 10 grams of Witte's peptone with tap water, adding 20 grams of the sugar or other compound to be examined, together with 10 grams of pure calcium carbonate, and making up the whole to 1 litre. In some cases, 2 grams of calcium phosphate were added, but no beneficial effect could be observed. Common salt is purposely omitted from the solution, because in its presence hydrochloric acid invariably passes over both into the volatile acids and the ethereal extract of the non-volatile acids.

The use of Witte's peptone alone has the further advantage that organisms of the Colon group have been found by direct experiment to grow freely in its solutions, without producing volatile acids, acids extractable by ether, or gaseous products in quantities large enough to interfere with the estimation of those produced from the compound under examination.

The action of the organism on the peptone, however, is undoubtedly modified by the presence of sugar, so that complete certainty on this point cannot be readily attained. This is shown by two facts.

1. In the presence of glucose, indole is not produced from peptone, whereas in its absence it is freely formed.

2. In the absence of sugar, practically no gas is evolved from peptone water, whereas in the presence of glucose the gas evolved invariably contains nitrogen, which must have been derived from the peptone. Thus in two experiments in which 250 c.c. of peptone water

were inoculated with this organism, no gas was evolved in one case and only 0·1 c.c. in the other, during a whole week, whilst indole was produced in both cases. On the other hand, a similar solution containing 2 grams of glucose gave about 100 c.c. of gas containing 7·5 per cent. of nitrogen. This result, which is in agreement with that obtained by other observers, is of great importance, since it throws some light on the function of the glucose in the nutrition of the organism.

The fermentations were in every case carried out in an atmosphere of nitrogen; the exact disposition of the apparatus and the methods of collecting and examining the gaseous products have been previously described in detail (*Trans. Jenner Inst.*, 1899, **2**, 126).

The method of analysis of the remaining products, which follows the general plan proposed by Nencki (*Centr. Bakt.*, 1891, **9**, 305) has, however, undergone considerable modification, and is therefore given in full.

Analytical Methods.

(1) *Residual Carbohydrate.*—Glucose and fructose were estimated by taking 50 c.c. of the clear liquid, adding excess of ammonium oxalate to precipitate the calcium, diluting to 100 c.c., and estimating the sugar present by means of Pavy's copper solution. In some cases, especially when beef broth was employed, the end of the reaction was rendered indistinct by the production of a purple coloration, due to the unaltered peptone and albumoses in the liquid. In such cases, it was found advisable to add four volumes of alcohol to some of the solution, filter an aliquot portion, evaporate off the alcohol, make up to the original bulk and then titrate for the sugar.

Mannitol was determined by Müller's method of measuring the change of rotation produced by the addition of a known weight of borax to the solution. The other substances present were found not to interfere with this measurement.

(2) *Total Acids.*—Fifty c.c. of the liquid were boiled for a short time with pure calcium carbonate, to effectually neutralise any free acid which might be present, and at the same time to remove calcium carbonate held in solution by carbonic acid. The dissolved calcium was estimated in the filtrate by precipitating with ammonium oxalate, and weighing as lime. The peptone, which was usually employed as the nutrient medium, contained calcium and was found to yield 0·106 gram of lime per 10 grams of peptone. This amount was therefore subtracted from the quantity found, in order to obtain the lime equivalent to the acids produced by the fermentation.

(3) *Alcohol.*—About 800 c.c. of the liquid were taken, 10 grams of oxalic acid added, the solution measured, and about 700—800 c.c. filtered off and distilled. The first 250 c.c. of the distillate were

reserved for the estimation of alcohol, and for this purpose were neutralised with normal alkali in presence of phenolphthalein paper, and then redistilled through a fractionating column; 100 c.c. of the distillate were collected and the alcohol calculated from the specific gravity.

(4) *Volatile Acids.*—The distillation of the acidified liquid was continued until only about 100 c.c. remained in the flask, and this was then distilled in steam until 100 c.c. of the distillate only required about 0·2 c.c. of normal alkali for neutralisation. In the presence of lactic acid, it is impossible to attain perfect neutrality, as this acid is itself slightly volatile with steam, the error thus introduced amounting to about 1 c.c. per litre of distillate. The distillate was then neutralised with normal alkali in presence of phenolphthalein, the residue from the alcohol distillation added, and the whole evaporated to dryness on the water-bath, redissolved in water, and diluted to 100 c.c.

In order to ascertain the nature of the acids present, three fractions were obtained by the addition of successive quantities of sulphuric acid and subsequent distillation, and the barium salts prepared from these were analysed. As numerous experiments showed that no higher acid than acetic was produced, this extended examination was not in every case carried out, but the formic acid was directly estimated by oxidation with mercuric chloride, and the acetic acid found by difference. The small amount of lactic acid present was neglected, as it was found that the only satisfactory method of estimating lactic acid—oxidation with alkaline permanganate and estimation of the oxalic acid produced (Ulzer and Seidel)—is inapplicable in the presence of acetic acid.

(5) *Lactic and Succinic Acids.*—The residue from the steam distillation was diluted to 150 c.c., and 25 c.c. were extracted with ether, which removes the lactic and succinic acids, together with some oxalic acid.

Since lactic acid is difficult to extract from aqueous solution, and the nutrient solutions tend to form an emulsion with the ether when shaken up by hand, it is convenient to employ some form of continuous extraction apparatus, and a modification of that described by Foerster (*Chem. Zeit.*, 1898, 22, 421) has been found very suitable.

The extraction was continued for 10 hours, at the close of which time experiment has shown that all the lactic acid is removed; the ether was then evaporated, and the liquid heated on the water-bath with excess of calcium carbonate for several hours. The lactic anhydride which is invariably formed when the ethereal extract is evaporated (Wislicenus) is thus completely converted into calcium lactate. The liquid was then filtered from the calcium oxalate and excess of

carbonate and diluted to 400 c.c.; 150 c.c. of this solution were taken for the estimation of the total acid present by precipitation of the calcium as oxalate.

Separation of Calcium Lactate from Calcium Succinate.—It was found that the principle of the method proposed by Müller for the separation of lactic from succinic acid by means of the difference in the solubility of their barium salts in dilute alcohol could also be applied to the calcium salts. Traces only of calcium succinate dissolve in 90 per cent. alcohol, whereas calcium lactate dissolves to the extent of about 3 grams in 100 c.c. of the liquid. The two salts can therefore be completely separated either by digesting the mixture of the dry salts with 90 per cent. alcohol, or, more conveniently, by dissolving the mixture in a measured volume of water and adding 9 volumes of alcohol. The following experiment, made to test the method, shows that the separation is practically complete.

0·7056 gram of calcium lactate yielded 0·1292 gram of lime.

0·7976 gram of the same salt was mixed with 0·1646 gram of pure calcium succinate, the whole treated with 90 per cent. alcohol, and the calcium estimated in the filtrate. This was found to yield 0·1468 gram of lime, whilst the amount calculated from the foregoing analysis of the lactate is 0·1460 gram.

The following method was therefore adopted for the separation and estimation of the succinic acid. One hundred and fifty c.c. of the solution of the calcium salts were evaporated to dryness on the water-bath in a beaker, the residue was dissolved in 10 c.c. of boiling water, and 90 c.c. of absolute alcohol were added. The liquid was allowed to stand for some time and then filtered, the precipitate washed with 90 per cent. alcohol, and the calcium estimated in the filtrate after the removal of the alcohol by distillation. This gives the equivalent of the lactic acid present, whilst the difference between this and the total acid gives the succinic acid. The precipitated calcium succinate can also be dissolved in water and the calcium in it estimated directly.

(6) *Determination of the nature of the Lactic Acid produced.*—The method usually employed for this purpose is to convert the acid into the zinc salt and estimate the amount of water of crystallisation and the optical rotation of this, the zinc salts of the active acids crystallising with $2H_2O$ (12·9 per cent.) and that of the inactive acid with $3H_2O$ (18·1 per cent.).

The zinc salts of the inactive and active acids, however, differ in solubility, and it is therefore impossible to prepare the salt from the acids obtained by extracting with ether in a state of purity, without to some extent altering the proportions in which the active and inactive acids are present. The presence of succinic acid, moreover, renders it essen-

tial to remove this substance from the lactic acid before the conversion of the latter into the zinc salt.

Attempts were therefore made to take advantage of the fact that the calcium salts of the active lactic acids have an optical rotation which is the opposite to that of the acids from which they are derived, and to estimate the amount of the active acid present from the change of rotation which occurs when the salt is converted into the acid.

This method suffers from two disadvantages (1) the lactic acids and their calcium salts have a very low specific rotation; (2) even in an aqueous solution of the acid there is a tendency towards the formation of an anhydride which has a much higher rotation than the acid, and in an opposite sense.

It was, however, found that by working in the manner described below, fairly consistent numbers could be obtained. The results given in the present paper are founded on the numbers obtained by the examination of a sample of calcium *d*-lactate derived from extract of meat, and the rotations were all measured on a Schmitt and Haensch saccharimeter which can be employed with lactic acid for relative determinations of this kind. The observations are being extended to specimens of pure *l*- and *d*-lactates resulting from the fractional crystallisation of zinc ammonium lactate, a supply of which I owe to the kindness of Prof. Purdie, and a full account of the absolute measurements and conditions and limits of accuracy will shortly be published. The numbers given in the present paper are probably accurate to about 5—10 per cent.

This method has the two advantages that a fair estimate of the nature of the whole of the lactic acid is obtained, and that the estimation can be carried out even in the presence of small amounts of optically active substances, such as proteid matter from the nutrient medium, or unfermented sugar, traces of which very frequently pass over into the ether extract in spite of the greatest care, owing to the character of the liquid to be extracted.

To carry out the estimation, the remainder of the 150 c.c. of the liquid left after the removal of the volatile acids by distillation is extracted with ether and the acid thus obtained converted into the calcium salt, which is then freed from calcium succinate in the manner already described, 10 c.c. of water and 90 c.c. of alcohol being used for each 1·5 grams of salt. The alcoholic filtrate is evaporated, decolorised if necessary with animal charcoal, and diluted so as to yield at least 30 c.c. of liquid. Five c.c. of the solution are taken for the estimation of the calcium, and from this the concentration of the solution is found. Two quantities of 12 c.c. are measured out and to one is added 1 c.c. of water, to the other 1 c.c. of aqueous hydrochloric acid containing sufficient acid to liberate the whole of the

lactic acid. Two solutions are thus obtained of the same concentration, one containing the acid and the other the calcium salt. These are then examined in the polarimeter and the difference between their rotations observed. The amount of lime as active acid corresponding to this difference is then found from the table and the relation of this to the total amount of lime present gives the percentage of active acid.

Action of Normal B. coli communis *on* d-*Glucose.*

The following table contains the results of five experiments, each carried out with peptone water, as already described, in an atmosphere of nitrogen, 20 grams of pure glucose being used.

Experiment No. 3 was carried out with a solution of ammonium sulphate containing 6·6 grams of this salt per litre, instead of peptone.

The gaseous products are expressed in c.c. per gram of sugar, and the other products in percentages of the weight of sugar fermented.

The organism employed in experiments 1, 2, and 3 was isolated from the stool of an adult, that employed in No. 6 from that of an unweaned child; and those used for Nos. 4 and 5 were isolated from the fæces of a dog and a rabbit respectively. The culture was made in every case into Parietti broth; the resulting growth was plated out, and cultures taken from a single colony. All the organisms gave the usual reactions for the normal bacillus.

Source of organism.	Sugar fermented. Grams.	Lactic acid.	Percentage of excess of *l*-acid in the lactic acid.	Acetic acid.	Alcohol.	Succinic acid.	Formic acid.	Carbon dioxide, per cent.	C.c. per 1 gram. Carbon dioxide.	C.c. per 1 gram. Hydrogen.
1. Adult.....	12·09	40·1	79	19·95	16·9	5·5	trace	—	—	—
2. ,, ...	20	31·9	not determined	18·84	12 85	(5·2)	none	18·09	91·8	110
3. ,, ...	20	40 1	,,	15·63	9·84	(6·7)	none	16·25	83	86
4. Dog	14·68	45·2	,,	14·14	8·9	(5·7)	none	12·55	65·2	79·9
5. Rabbit ...	11 63	44·4	75	19·69	10 2	4 6	1·4	12 1	61·6	80·7
6. Child	13·33	46·0	95	12·02	10·9	5·7	2·5	—	—	—

These results illustrate the degree of variation which is found in the action of these organisms. Even parallel experiments, carried out with the same culture under apparently identical conditions, have frequently been found to yield the various products in somewhat different proportions. The weight of lactic acid produced varies from 31·9 to 46 per cent., but never exceeds 50 per cent. of the sugar employed. In every case, this acid consists of a mixture of inactive acid with a preponderating amount of *l*-acid. In spite of this result however, the production of *l*-lactic acid cannot be taken as an essential function of this organism, since the production of the *d*-acid has been frequently observed by various authors, employing this bacillus derived

from various sources. It has also been found by Péré (*Ann. Inst. Past.*, 1898, 12, 63; 1893, 7, 737) that some of these organisms may be made to yield either *d*- or *l*-lactic acid, according to the conditions of nourishment, whilst others yield the same acid under all conditions.

These numbers do not, in every case, account for the whole of the sugar, there being a deficit amounting to from 1/12th to 1/8th of the total carbon, but a careful search has not yet revealed the nature of the change which this remaining portion has undergone. It is possible that a portion of the sugar is reduced either by the hydrogen which is evolved, or by a reaction in which a molecule of water, or perhaps of formic acid, intervenes. Sorbitol, which might be thus produced, is not easily fermented by the organism, and might remain unaltered and escape notice. Further experiments are still in progress with the object of deciding this question.

A clearer view of the nature of the chemical change is afforded by expressing the results in terms of the carbon atoms of the original sugar. This is done in the following table:

Source of organism.	Carbon atoms as					Hydrogen atoms.
	Lactic acid.	Acetic acid.	Alcohol.	Succinic acid.	Carbon dioxide and formic acid.	
1. Adult	2·40	1·2	1·32	0·34	—	—
2. ,, ...	1·91	1·13	1·01	0·32	0·74	1·77
3. ,, ...	2·40	0·94	0·98	0·41	0·67	1·39
4. Dog	2·71	0·84	0·70	0·35	0·53	1·29
5. Rabbit	2·67	1·18	0·80	0·29	0·50	1·30
6. Child	2·76	0·81	0·85	0·35	—	—

This reveals the fact that whilst the lactic acid accounts for 2—3 of the carbon atoms of the original molecule, the alcohol and acetic acid are formed in nearly equivalent amounts, and each accounts for only one carbon atom of the sugar molecule. The amount of carbon dioxide obtained in different experiments represents less than 1 carbon atom, but never falls below 0·5. The ratio of hydrogen to carbon dioxide is not exactly 1 : 1 by volume, but does not depart widely from this ratio. The production of about half the weight of the sugar as lactic acid, and of acetic acid and alcohol in equivalent amounts, each corresponding to about 1 carbon atom of the sugar molecule, may be represented by a very simple equation, which, however, somewhat overestimates the amounts of carbon dioxide and hydrogen which are actually found:

$$2C_6H_{12}O_6 + H_2O = 2C_3H_6O_3 + C_2H_4O_2 + C_2H_6O + 2CO_2 + 2H_2.$$

It seems probable, however, that this represents the main reaction, but is subject to modification by secondary changes (see p. 626).

In solutions containing beef broth, as already mentioned, the products derived from the sugar cannot be distinguished accurately from those previously present in the broth and formed from it by the action of the organism. The lactic acid obtained in this medium is invariably much less active, and sometimes quite inactive, as has been pointed out in a previous paper (*Trans. Jenner Inst.*, 1899, 2, 126). This is, at all events in part, to be ascribed to the presence of *d*-lactic acid in the broth, since this acid is not affected by the organism (p. 625). Precisely similar relations are found with lævulose and mannitol.

The Fermentation of Glucose by Bacillus typhosus.

The products of fermentation of glucose by *B. typhosus* are very similar in character to those produced by *B. coli communis*, the only essential difference being that formic acid is produced in large quantity, instead of only in traces. This formic acid doubtless represents the carbon dioxide and hydrogen which are produced by *B. coli communis*, the *B. typhosus* being unable to decompose formates, whilst *B. coli communis*, as will be shown later on, has this power (see also Pakes and Jollyman, this vol., p. 386). The fermentation is not a very vigorous one, and in all cases terminated when about half of the sugar had been decomposed.

The two following experiments were carried out with cultures of virulent typhoid in an atmosphere of nitrogen. The solutions were sterilised at 80° for an hour before being examined:

	I.		II.	
	Per cent.	Carbon atoms.	Per cent.	Carbon atoms.
Lactic acid.....	31·1	1·87	49·5	2·96
Acetic acid.....	16·1	0·97	12·7	0·76
Alcohol	10·6	0·83	9·1	0·70
Succinic acid	2·1	0·13	trace	trace
Formic acid.....	17·2	0·67	17·7	0·69

In both cases, a mixture of inactive with *l*-lactic acid was formed; that produced in experiment I was found to contain 47·5 per cent. of the active acid, this being a smaller proportion than is produced by the *B. coli communis*.

Action of Abnormal Forms of B. coli communis *on Glucose.*

Only three of these organisms have so far been employed: 1. Two organisms which differed from the normal only in not curdling milk until after the expiration of 7 or 8 days. One of these (A) was isolated from the fæces of a guinea-pig, and the second (B) from those of a pigeon.

2. An organism (C) which I owe to the kindness of Dr. Gordon, who had isolated it from sewage. This organism gave no gas with sugar solutions, but curdled milk and produced indole in the normal manner.

The results are stated both in percentages and in terms of the carbon atoms of the sugar molecule.

	A.		B.		C.	
	Per cent.	Carbon atoms.	Per cent.	Carbon atoms.	Per cent.	Carbon atoms.
Lactic acid	33·2	1·99	25·4	1·52	76·6	4·6
Succinic acid	3·2	0·2	3·9	0·24	3·3	0·2
Acetic acid	20·95	1·26	24·5	1·47	14·1	0·85
Alcohol	14·33	1·12	20·1	1·57	4·6	0·36
Formic acid	1·4	0·06	3·4	0·13	9·0	0·35
Carbon dioxide ...	14·6	0·60	18·5	0·76	none	none
Per cent. of active *l*-acid	64·4		80		32	

It appears from this that organisms A and B do not differ essentially from the normal *B. coli communis* in their action on glucose, although they yield rather less lactic acid and more alcohol and acetic acid (see p. 618).

The organism C, on the other hand, differs distinctly in its mode of action, both from *B. coli communis* and *B. typhosus*. The amount of lactic acid is greater, and the proportion of active acid less, whilst the alcohol and acetic acid are produced in different proportions. Like *B. typhosus*, this organism produces formic acid, which it appears to be unable to decompose.

This result shows that an organism which appears by its cultural tests to be closely related to the colon bacillus and to *B. typhosus*, may nevertheless differ from both of these in its action on glucose.

Action of B. coli communis *on Lævulose* (d-*Fructose*).

Lævulose is readily fermented by this organism, both in peptone water and in peptone beef broth. The products are identical in character with those produced from glucose. The following results were obtained in peptone water; 20 grams of the sugar containing 0·8 gram of water, and 19·2 grams of lævulose were employed:

	I.		II.	
	Per cent.	Carbon atoms.	Per cent.	Carbon atoms.
Lactic acid	43	2·58	48·2	2·89
Succinic acid	not determined		6·1	0·37
Alcohol	,,	,,	11·5	0·90
Acetic acid	13	0·78	16·1	0·97
Carbon dioxide ...	15·5	0·63	13·07	0·53
Formic acid	—	—	trace	

The lactic acid produced in both cases was lævorotatory. That derived from experiment I was not further examined. That obtained from experiment II was converted into the zinc salt. As this was found to contain succinic acid, the lactic acid was re-extracted, converted into the calcium salt, and the latter purified and examined as usual. It was found to contain 90 per cent. of the active *l*-lactic acid.

An experiment which was carried out in peptone beef broth yielded a very similar result to experiments with glucose under the same conditions. The lactic acid obtained was greater in quantity (65 per cent.), and contained only 51 per cent. of active acid. As is the case with glucose in this medium, the sum of the products exceeded the weight of the sugar taken.

The difference of constitution between glucose and lævulose, therefore, does not appear to produce any difference in the character of the products of fermentation by this organism. The lactic acid in particular is of the same character, and this shows that the configuration of the lactic acid produced does not depend on that of the carbon atom situated in the α-position to the aldehyde group of glucose, since in lævulose this atom is not asymmetric.

Action of B. coli communis *on Mannitol.*

Although the substitution of lævulose for glucose produces no recognisable difference in the products of fermentation, a very marked

change is observed when the sugar is replaced by a hexatomic alcohol.

Dulcitol is not fermented by this organism. The attempt was made in peptone water, and although the organism developed well, no sign of fermentation (gas evolution, or production of acid) could be observed. A similar power of discriminating between mannitol and dulcitol has previously been observed in other organisms.

Sorbitol appears to undergo only a very slight fermentation when submitted to this organism, and the products have not yet been examined.

Mannitol, on the other hand, is very vigorously and completely acted on, the products being qualitatively the same as those produced from glucose and lævulose.

The following are the complete results of two experiments, I in peptone water, II in beef broth:

	I.		II.	
	Per cent.	Carbon atoms.	Per cent.	Carbon atoms.
Lactic acid	18·6	1·13	24·9	1·51
Succinic acid[1].....	8·9	0·55	9·4	0·58
Acetic acid[2].....	9·5	0·58	8·2	0·50
Alcohol	28·06	2·22	33·5	2·65
Formic acid	3·0	0·12	0·6	0·02
Carbon dioxide ...	28·44	1·16	30·84	1·26
Per cent. of active *l*-acid	79		29	
Hydrogen (atoms)	2·7		2·7	

The lactic acid from experiment I was first converted into the zinc salt, and this was then treated with pure lime, and the resulting calcium salt purified and examined in the usual manner.

The experiment in beef broth, as usual, yields high results, whilst the lactic acid is less active.

The most noticeable point about this result is the large yield of alcohol, which considerably exceeds 25 per cent. of the weight of the mannitol fermented. It is always produced in this large proportion, two other experiments giving 28·2 per cent. (peptone water) and 26·9 per cent. (sodium asparaginate). When separated by means of potassium carbonate, dried over the same salt and distilled, it boiled constantly at 78°, and was therefore pure ethyl alcohol. The succinic

acid is much larger in amount than that obtained from glucose, whilst the lactic and acetic acids are much smaller. The amount of hydrogen evolved is also greater, the total amount, including that of the undecomposed formate, being nearly three atoms of that contained in the mannitol. The fact that the amount of alcohol corresponds with two of the carbon atoms of the mannitol, whereas glucose only yields one of its carbon atoms as alcohol, seems to be definitely connected with the fact that in mannitol there are two groups of the formula $CH_2(OH)\cdot CH(OH)\cdot$, whilst in glucose only one such group occurs.

The view that the alcohol produced originates from this particular group is strikingly confirmed by the action of this organism on glycerol, $CH_2(OH)\cdot CH(OH)\cdot CH_2\cdot OH$. Quite recently, I have found that the chief products of this action are alcohol and formic acid, or its decomposition products, carbon dioxide and hydrogen, only a very small quantity of other acids being produced.

$$C_3H_8O_3 = C_2H_6O + CH_2O_2.$$

5·2 grams of glycerol yielded 2·4 grams of alcohol, 1·8 grams of formic acid (partially as carbon dioxide and hydrogen), together with small amounts of two other acids, probably acetic acid and succinic acid.

Reduction of Asparaginic Acid by B. coli communis *in presence of Glucose and Mannitol.*

When the sole nitrogenous nourishment supplied to this organism consists of sodium asparaginate, glucose and mannitol are fermented in the usual manner, with the single exception that the amount of hydrogen evolved is much less, a large proportion of it serving to reduce the asparaginic acid to ammonium succinate.

$$CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO_2H + 2H = CO_2H\cdot CH_2\cdot CH_2\cdot CO_2H + NH_3.$$

This is shown in the following table of results, in which col. I gives (*a*) the volume of hydrogen actually evolved; (*b*) the volume of hydrogen taken up by the asparaginic acid, calculated from the ammonia found in the solution, and (*c*) the volume of hydrogen evolved in another experiment in presence of peptone from the same weight of glucose. Col. II gives the same information for mannitol. The solutions contained 20 grams of sodium asparaginate and 20 grams of glucose and mannitol respectively per litre.

	I. Glucose.		II. Mannitol.	
	c.c.		c.c.	
a.	663	1884	887	2925
b.	1221		2038	
c.	1776		3274	

The occurrence of this reduction is of some interest, since asparaginic acid is not very easily reduced by ordinary reagents, but requires to be heated with hydriodic acid. Whether the reduction is due to a purely chemical reaction or whether the protoplasm of the organism plays a direct part in the reduction must remain at present undecided.

The reduction is also interesting from another point of view, as showing that an organism like *B. coli communis*, which has very little direct action on proteids, may, nevertheless, under appropriate circumstances, assist in the process of still further decomposing the products formed from them by putrefaction.

Experiments made with aminoacetic and aminopropionic acids to ascertain whether a similar reduction occurred gave negative results, the growth of the organism being very feeble and no ammonia being formed.

Action of B. coli communis *on* d-*Galactose and* l-*Arabinose.*

Both of these sugars are fermented by this organism, with formation of the same products as are derived from glucose. The complete course of the action is still under investigation, but it may be stated that both yield a mixture of *l*-lactic acid with the inactive acid. *l*-Arabinose, moreover, yields alcohol and acetic acid in about the same molecular proportion as glucose, whilst the amount of lactic acid is only half as great.

Action of B. coli communis *on Formates and Lactates.*

The fact that *B. coli communis* differs in its action on glucose from *B. typhosus*, mainly by the production of carbon dioxide and hydrogen instead of formic acid, led to experiments on the direct action of the former organism on formates. It was found that this organism effects the decomposition of these salts according to the equation

$$H{\cdot}CO_2Na + H_2O = NaHCO_3 + H_2.$$

Hoppe-Seyler, in 1876, described a decomposition of this kind by the action of the bacteria of sewage, and quite recently Messrs. Pakes and Jollyman (this vol., p. 386) have drawn attention to this function of *B. coli communis* and other organisms.

The particular organism employed in these experiments exerted comparatively little action on a solution containing 2 per cent. of sodium formate and 1 per cent. of Witte's peptone. In presence of a small amount of sugar, however, a much larger amount of the formate was decomposed, as is shown in the following table, the hydrogen due to the sugar being deducted:

Sodium formate	2 per cent.	2 per cent.	2 per cent.
Glucose	0 ,,	0·2 ,,	0·4 ,,
Hydrogen evolved ...	105 c.c.	1122 c.c.	1481

Increase of pressure appears to favour the formation of formic acid instead of its decomposition products. Thus, under an additional pressure of 0·5 atmosphere, the amount of formic acid produced was increased in one case 3 times, and in a second experiment 10 times.

Pressure.	C.c. of *N*-formic acid from 1 gram of glucose.
1 atmosphere.	0·15
1·5 ,,	0·42
1·5 ,,	1·32

This organism has practically no action on inactive lactic acid in the form of ammonium, calcium, or sodium salt, and even when a small amount of glucose is added, the amount of active lactic acid produced is not greater than is produced from the sugar alone. Thus, a 2 per cent. peptone solution, containing 9 grams of lactic acid as sodium salt, together with 1·8 grams of glucose, only yielded 0·4 gram of active lactic acid, the whole of which is derived from the sugar.

This fact is important as showing that the active lactic acid which results from the action of the organism on so many sugars is almost certainly not formed by the selective decomposition of previously formed inactive acid.

Theoretical Considerations.

The results communicated above seem to show that in the fermentation of *d*-glucose and *d*-fructose, at least two molecules are concerned, and that the chief reaction may be best represented by the equation

$$2C_6H_{12}O_6 + H_2O = 2C_3H_6O_3 + C_2H_4O_2 + C_2H_6O + 2CO_2 + 2H_2,$$

which finds a simple diagrammatic expression as follows :

$$\begin{array}{l} CH_2{\cdot}OH \\ | \\ CH{\cdot}OH \quad CH_2{\cdot}OH \\ | \\ \cdots\cdots\cdots\cdots\cdots \\ CH{\cdot}OH \quad CH{\cdot}OH \\ | \quad\quad | \\ CH{\cdot}OH \quad CH{\cdot}OH \\ | \quad\quad | \\ CH{\cdot}OH \quad CH{\cdot}OH \\ | \\ \cdots\cdots\cdots\cdots\cdots \\ CHO \quad\quad CH{\cdot}OH \\ \quad\quad\quad\quad | \\ \quad\quad\quad\quad CHO \end{array} = CH_3{\cdot}CH_2{\cdot}OH + CO_2 + H_2$$

$$+ H_2O = CH_3{\cdot}CO_2H + CO_2 + H_2.$$

According to this scheme, two groups, ·CH(OH)·CH(OH)·CH(OH)·, are left, which may then be converted into lactic acid or partly break down into other compounds, among which alcohol, acetic acid, hydrogen, and succinic acid are probably to be numbered. This secondary change probably accounts for the fact that in some cases (experiments A and B, p. 620), whilst the lactic acid represents considerably less than 3 atoms of carbon, the alcohol and acetic acid are correspondingly larger in amount.

In the case of mannitol, the fact that the presence of two ·CH_2(OH)·CH(OH)· groups gives rise to a largely increased yield of alcohol and a decreased yield of acetic acid, must certainly be considered significant. The chief reaction in this case may also be most easily imagined as embracing two molecules:

$$\begin{array}{l} CH_2\cdot OH \\ | \\ CH\cdot OH \quad CH_2\cdot OH \\ | \qquad\quad | \\ CH\cdot OH \quad CH\cdot OH \\ | \qquad\quad | \\ CH\cdot OH \quad CH\cdot OH \\ | \qquad\quad | \\ CH\cdot OH \quad CH\cdot OH \\ | \qquad\quad | \\ CH_2\cdot OH \quad CH\cdot OH \\ \qquad\qquad | \\ \qquad\quad CH_2\cdot OH \end{array} = CH_3\cdot CH_2\cdot OH + CO_2 + H_2$$

$$= CH_3\cdot CH_2\cdot OH + CO_2 + H_2 .$$

The two residual groups, ·CH(OH)·CH(OH)·CH(OH)·, then behave in an analogous manner to those derived from the sugars, but yield in this case less lactic acid and more of the other products.

From this point of view the action of the organism on a pentose like *l*-arabinose is of great interest. If the action is of the same type as that on glucose, fructose, and mannitol, the maximum yield of lactic acid should only be 30 per cent. of the weight of the sugar, only three carbon atoms from two molecules being available for the production of the acid, whereas in the case of glucose six atoms are available:

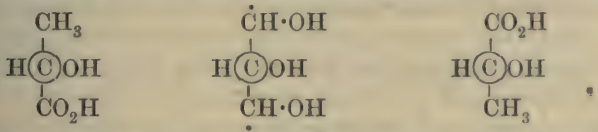
$$\begin{array}{l} CH_2\cdot OH \\ | \\ CH\cdot OH \quad CH_2\cdot OH \\ | \qquad\quad | \\ CH\cdot OH \quad CH\cdot OH \\ | \qquad\quad | \\ CHO \qquad CH\cdot OH \\ \qquad\qquad | \\ \qquad\quad CHO \end{array}$$

The acetic acid and alcohol, on the other hand, should represent each one carbon atom per molecule of the sugar. The single experiment

so far completed is in good agreement with this scheme, the amounts of alcohol and acetic acid formed bearing nearly the required ratio to the lactic acid, but the experiment must be multiplied before any definite conclusion can be drawn.

The group ·CH(OH)·CH(OH)·CH(OH)·, from which it is suggested that the lactic acid is formed, has the same empirical composition as lactic acid, and would yield this acid by the interchange of a hydrogen and oxygen atom between the two terminal groups, or between the terminal groups of a second similar chain derived from another molecule of the sugar.

The unaltered asymmetric group, ·CH(OH)·, would then retain its asymmetry in the new molecule of lactic acid thus produced. Such a rearrangement, however, if it could be effected by means of reagents containing only symmetric molecules, would probably result in the production of an inactive acid, the oxidation and reduction taking place to an equal extent at either end of the chain.



The change being, however, brought about in the presence of the asymmetric molecules of the protoplasm of the organism—or possibly of an enzyme—would most probably be influenced so as to proceed entirely in one direction, or more rapidly in one direction than in the other, and thus give rise to an active acid, the activity of which would be independent of the previous configuration of the group and depend only on the nature of the organism. This view is therefore not inconsistent with the fact observed by Péré that the same sugar when submitted to the same organism, but under different conditions of nourishment, may yield lactic acids of opposite signs. Before admitting this explanation, it would, however, be necessary to show that the type of reaction had remained unaltered.

The question of the origin of the lactic acid within the molecule of the sugar may also be attacked by examining the products formed from sugars of different configuration, and the work is being proceeded with in this direction ; it is also being extended to embrace a study of the various other types of formation of lactic acid from the carbohydrates, and the action of these organisms on compounds of different constitution.

Summary of Results.

1. In the fermentation of glucose by *B. coli communis*, the lactic acid produced never exceeds in amount one half of the sugar fermented, but may be less. It is optically active, but is probably not derived from previously formed inactive acid. Alcohol and acetic acid are produced in approximately equivalent amounts.

2. The products of fermentation of glucose by *B. typhosus* are similar to those produced by *B. coli communis*, with the exception that formic acid is produced instead of a mixture of carbon dioxide and hydrogen.

3. Certain bacteria which appear by the ordinary tests to be intermediate between *B. coli communis* and *B. typhosus* decompose glucose according to a different type of reaction.

4. *d*-Fructose, when fermented by *B. coli communis*, yields the same products as glucose, and in the same proportion.

5. Mannitol, when fermented by *B. coli communis*, yields about 28 per cent. of alcohol, corresponding to two of its carbon atoms, together with less lactic acid and acetic acid than are formed from glucose. The alcohol appears to be produced from the group $CH_2(OH)\cdot CH\cdot OH$.

6. Asparaginic acid is reduced to ammonium succinate by *B. coli communis* in presence of glucose or mannitol, the volume of hydrogen evolved being correspondingly diminished.

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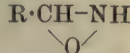
LXV.—*The Action of Alkyl Haloids on Aldoximes and Ketoximes. Part II. Alkylated Oximes and* iso-*Oximes, and the Constitution of Aliphatic Oximes.*

By WYNDHAM R. DUNSTAN and ERNEST GOULDING.

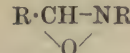
IN a previous paper (Trans., 1897, 71, 573) we have shown that by the direct action of alkyl iodides on aldoximes and ketoximes, alkyl derivatives are obtained in which the alkyl group is joined to the nitrogen atom, the true ethers of the oximes not being formed under these conditions. The cases investigated were formaldoxime, acetaldoxime, acetoxime, and acetophenoxime, whilst that of benzaldoxime had been previously examined at the suggestion of one of us by Luxmoore (Trans., 1896, 69, 183). It is already known that in the presence of sodium methoxide, certain oximes furnish chiefly the isomeric ethers in which the alkyl group is joined to oxygen, but these derivatives in

the aliphatic series are at present little known. Beckmann (*Ber.*, 1889, **22**, 429) obtained the first of the alkyl nitrogen derivatives from benzaldoxime, whilst Goldschmidt (*Ber.*, 1890, **23**, 2163) showed that aromatic oximes sometimes furnish both isomerides when acted upon by an alkyl iodide in the presence of sodium methoxide.

In the present paper, we give an account of the action of several alkyl iodides on representative aldoximes and ketoximes in the presence of sodium methoxide. We show that under these circumstances both isomerides are invariably produced, the quantity of each depending on the nature of the oxime and of the alkyl iodide used. We give an account of the properties and reactions of the alkyl-nitrogen and alkyl-oxygen derivatives of acetoxime, acetophenoxime, and acetaldoxime, obtained through the action of methyl, ethyl, and propyl iodides in the presence of sodium methoxide. We prove that the one set of derivatives in which the alkyl group is joined to nitrogen (sometimes clumsily designated "nitrogen ethers") are to be regarded as derived from an isomeric or tautomeric *iso*oximido-form of the oximes, that is, for aldoximes,

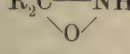


*iso*Aldoxime.

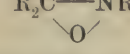


Alkyl*iso*aldoxime.

and for ketoximes,



*iso*Ketoxime.



Alkyl*iso*ketoxime.

On hydrolysis, these derivatives furnish the corresponding aldehyde or ketone, and a β-substituted hydroxylamine, $CH_3\cdot CH(O)N\cdot CH_3 + H_2O = CH_3\cdot CHO + \tilde{N}(CH_3)H\cdot OH$, whilst on reduction by the usual methods they furnish an amine of the substituted alkyl group, and again the aldehyde or ketone. If special precautions are taken in effecting the reduction, the corresponding secondary amines are obtained. It is remarkable, as was pointed out in our previous paper, that these compounds in which the alkyl groups are joined to nitrogen are extremely unstable, and are usually obtained in combination with sodium iodide. Attempts to free them from combination with sodium iodide in the presence of water usually leads to immediate hydrolysis.

On the other hand, the true ethers have been obtained in the free state as liquids possessing considerable stability. They behave as derivatives of the ordinary oxime in which the alkyl replaces the hydrogen in the hydroxyl group, and is consequently in union with oxygen.

$R\cdot CH{:}N\cdot OH$	$R\cdot CH{:}N\cdot OR^1$
Aldoxime.	Alkyl ether.
$R_2C{:}N\cdot OH$	$R_2C{:}N\cdot OR^1$
Ketoxime.	Alkyl ether.

Their hydrolysis, which is more difficult to accomplish than that of their isomerides, results in the production of an aldehyde or ketone and an α-substituted hydroxylamine, $CH_3\cdot CH{:}N\cdot OCH_3 + H_2O = CH_3\cdot CHO + NH_2\cdot OCH_3$. Corresponding products are obtained on reduction.

The fact that, under the conditions described, two varieties of alkyl derivatives may be obtained from aldoximes and ketoximes strongly supports the view that these oximes are capable, under certain conditions, of existing in tautomeric or isomeric forms corresponding with the general formulæ given above, a view to which we have already called attention.

The observation that the direct action of an alkyl haloid on an oxime results in the production of the alkyl *iso*oxime, leads to the conclusion that the *iso*oximido- is probably the normal configuration of an oxime, the oximido-form being induced by the presence of alkali, and probably determined by the formation of a "salt." The facility with which these metallic derivatives are dissociated accounts for the fact that the isomeric alkyl *iso*oximes are also produced in presence of sodium methoxide, no doubt by direct action of the alkyl iodide on the regenerated oxime.

*Action of Methyl Iodide on Acetoxime in presence of Sodium Methoxide. Methylacetoxime and Methyl*isoa*cetoxime.*

9·2 grams of sodium were dissolved in methyl alcohol, and a solution of acetoxime (29·2 grams) was added. Methyl iodide (56·8 grams) was gradually introduced into the mixture contained in a flask connected with a reflux condenser. Action occurred at once with considerable rise in temperature. When the whole of the methyl iodide had been added, and the vigorous action had subsided, the flask was heated on the water-bath for half-an-hour.

The product was now distilled. The first fraction (about 30 c.c.), which was collected separately, contained a substance of fragrant odour, which proved to be the *methyl ether of acetoxime*, $(CH_3)_2C{:}N\cdot OCH_3$. In order to isolate this compound, the distillate was saturated with powdered calcium chloride, and after standing for 24 hours was distilled. The distillate was again mixed with calcium chloride and redistilled. The final product thus obtained was a colourless, mobile liquid of characteristic odour, which boiled at 72—72·5°. The yield

of this compound is very small, and does not amount to much more than 6—7 per cent. of the acetoxime employed.'

Acetoxime methyl ether is fairly soluble in water, and mixes with alcohol and ether in all proportions. Its aqueous solution is neutral to litmus.

When the methyl ether is dissolved in a very small quantity of an alcoholic solution of hydrogen chloride, and platinic chloride is added, the *platinichloride* separates immediately in small, prismatic needles; on recrystallising this salt from alcohol by the addition of ether, it forms well-defined hexagonal prisms with pointed ends which deliquesce in air.

0·0811 gave on ignition 0·0268 Pt. Pt = 33·1.

$[(CH_3)_2C{:}N{\cdot}OCH_3]_2,H_2PtCl_6$ requires Pt = 33·2 per cent.

When heated with hydrochloric acid (10 per cent.) for an hour in a flask attached to a reflux condenser, the substance is hydrolysed with the formation of acetone and α-methylhydroxylamine.

$$(CH_3)_2C{:}N{\cdot}OCH_3 + H_2O = (CH_3)_2CO + NH_2{\cdot}OCH_3.$$

On evaporating the product to dryness, a residue was obtained which completely dissolved in alcohol, and on the addition of ether to the alcoholic solution, the hydrochloride of α-methylhydroxylamine separated in pearly scales melting at 148°, which did not reduce Fehling's solution. Some of this salt was reduced by warming it with zinc and hydrochloric acid; the product was made alkaline by the addition of solution of soda, and the liberated base distilled into dilute hydrochloric acid. Upon evaporating the acid distillate to dryness, a white, crystalline residue was obtained, insoluble in alcohol, and possessing the characters of ammonium chloride. The platinichloride was prepared and analysed.

0·2563 gave 0·1133 Pt. Pt = 44·2.

$(NH_4Cl)_2PtCl_4$ requires Pt = 43·9 per cent.

It is evident, therefore, that the salt is α-methylhydroxylamine hydrochloride, and that the compound which furnished it on hydrolysis is the methyl ether of acetoxime, $(CH_3)_2C{:}N{\cdot}OCH_3$.

The product of the reaction from which the ether and some of the methyl alcohol had been distilled crystallised on cooling in long, colourless needles. On examination, these were proved to be a compound of sodium iodide with methyl*iso*acetoxime, $(CH_3)_2C\!\!<\!\!\begin{matrix}\text{N}\cdot CH_3\\ \text{O}\end{matrix}\!\!>\!\!,NaI$,

corresponding to the similar compound of methyl*iso*-β-*m*-nitrobenzaldoxime which has been described by Goldschmidt and Kjellin (*Ber.*, 1891, **24**, 2808). It was collected, drained on a porous tile, dried in the desiccator, and recrystallised from hot methyl alcohol.

0·5243 gave 0·5187 AgI. I = 53·5.
0·3471 yielded 0·02065 N (as ammonia). N = 5·95.
$(CH_3)_2C\overset{O}{\diagdown\diagup}N\cdot CH_3,NaI$ requires I = 53·6. N = 5·91 per cent.

This substance is deliquescent and very readily soluble in water; it also dissolves in methyl and ethyl alcohols, but is insoluble in ether. It melts at 206° with decomposition. When warmed with dilute acid or boiled with water, it is quickly hydrolysed with the production of acetone and β-methylhydroxylamine,

$$(CH_3)_2C\overset{O}{\diagdown\diagup}N\cdot CH_3 + H_2O = (CH_3)_2CO + NH(CH_3)\cdot OH.$$

An aqueous solution of the compound was distilled; the distillate contained acetone and an alkaline base which strongly reduced Fehling's solution. The liquid was acidified with hydrochloric acid and evaporated to dryness on the water-bath. The residue possessed all the characters of β-methylhydroxylamine hydrochloride, crystallising in long extremely hygroscopic needles, which melted at about 85°; on reduction with zinc and hydrochloric acid, it furnished methylamine.

When the substance is boiled with hydriodic acid, it is hydrolysed and the β-methylhydroxylamine is immediately reduced to methylamine. The methylamine was obtained as the hydrochloride, and the platinichloride prepared and analysed.

0·1239 gave 0·0513 Pt. Pt = 41·4.
$(NH_2\cdot CH_3)_2,H_2PtCl_6$ requires Pt = 41·3 per cent.

In another experiment, some of the sodium iodide compound of the methyl derivative was dissolved in water, zinc dust added, and then very dilute hydrochloric acid in small quantities at a time. The base was liberated in the usual way and identified as methylamine by means of the platinichloride.

0·0726 gave 0·0301 Pt. Pt = 41·5 per cent.

Acetone, but no trace of any other amine than methylamine, could be detected, and it therefore seems probable that reduction occurs thus:

$$(CH_3)_2C\overset{O}{\diagdown\diagup}N\cdot CH_3 + H_2 = (CH_3)_2CO + NH_2\cdot CH_3.$$

If a solution of iodine in strong hydriodic acid is added to a solution of the sodium iodide compound in methyl alcohol (in approximately the proportions required to form the periodide) and the mixture evaporated nearly to dryness on the water-bath, a residue is obtained consisting of sodium iodide and crystals showing a fine beetle-green

lustre; the latter may be extracted with chloroform and purified by repeated crystallisation from the same solvent. Analysis shows that this compound is the periodide of methyl*iso*acetoxime previously obtained by us (Trans., 1897, 71, 577) by the direct action of methyl iodide on acetoxime. We have shown that the formula of this compound is $[(CH_3)_2C\!\!<\!\!\!\!>\!\!N\cdot CH_3,HI]_2I$.

Many attempts have been made to separate the methyl derivative from the sodium iodide compound, but hitherto without success on account of the facility with which it suffers hydrolysis immediately it is liberated in the presence of water.

Action of Ethyl Iodide on Acetoxime. Ethylacetoxime and Ethyliso-acetoxime.

When acetoxime, dissolved in methyl alcohol, is mixed with the calculated quantity of sodium methoxide and ethyl iodide, a vigorous reaction occurs, so much heat being developed that it is necessary to cool the flask. When the action has subsided, the flask is heated on the water-bath for half-an-hour with an upright condenser attached.

The *ether* passes over on distillation with the first fraction of methyl alcohol, and being almost insoluble in water it can be obtained from the alcoholic distillate by the addition of water, when it rises to the surface as a colourless mobile oil. It is separated and dried with calcium chloride. The usual yield of this substance is about 20 per cent. It has a pleasant ethereal smell, boils at 91·5—92·5°, and is miscible with alcohol and ether in all proportions. The *platinichloride* was prepared in a similar manner to that of the methyl ether. The crystals which first separated were washed with a mixture of alcohol and ether, redissolved in a small quantity of warm alcohol, and recrystallised by the addition of ether. The salt forms long, rectangular prisms of a fine orange colour.

It is deliquescent and extremely soluble in water, readily soluble in alcohol, but insoluble in ether.

0·1102 gave 0·0352 Pt. Pt = 31·9.

$[(CH_3)_2C{:}N\cdot OC_2H_5]_2,H_2PtCl_6$ requires Pt = 31·8 per cent.

The concentrated liquid from which the ethyl oxime had been distilled was transferred to an evaporating dish; on standing in the desiccator, crystals of sodium iodide slowly separated. The mother liquor was decanted from these, and further concentrated in a vacuum when a mass of needle-shaped crystals suddenly formed, which analysis has shown to consist of a compound of ethyl*iso*acetoxime with sodium iodide, $(CH_3)_2C\!\!<\!\!\!\!>\!\!N\cdot Et,NaI$.

This substance exhibits all the usual characters of these compounds; on hydrolysis, it yields acetone and β-ethylhydroxylamine; it is hygroscopic and deliquescent and very soluble in water and in alcohol. When reduced with zinc dust and hydrochloric acid as in the previous case, it yields ethylamine. This was identified by preparing the hydrochloride and platinichloride; the latter salt was analysed, with the following result:

0·0506 gave, on ignition, 0·0198 Pt. Pt = 39·1.

$(NH_2 \cdot C_2H_5)_2,H_2PtCl_6$ requires Pt = 39·0 per cent.

*Action of Propyl Iodide on Acetoxime. Propylacetoxime and Propyl-*iso*acetoxime.*

When propyl iodide is added to the calculated quantity of solution of sodium acetoxime in methyl alcohol, the action does not take place so vigorously as when methyl and ethyl iodides are used, and less heat is evolved. In order to complete the reaction, the solution is heated for about 3 hours on the water-bath. About two-thirds of the alcohol is now distilled off, and this carries the propylacetoxime with it; on the addition of water, the latter is thrown out of solution and rises to the surface as a colourless, sweet-smelling oil. It is separated and dried with calcium chloride. When heated in a paraffin bath, it distils almost constantly at 116·5°. The yield is about 20 per cent.

The concentrated solution from which the propylacetoxime has been distilled is dark coloured. When evaporated in a vacuous desiccator, sodium iodide crystallises out and a very viscous liquid remains, which possesses a carbamine-like odour (due probably to some decomposition). When hydrolysed with dilute acid, it yields acetone and a base possessing powerful reducing properties, which is doubtless β-propylhydroxylamine. This liquid could not be crystallised. It was, however, without doubt the sodium iodide compound of propyl*iso*acetoxime, for when reduced with zinc and hydrochloric acid, a base was obtained which furnished a hydrochloride possessing the appearance and general properties of propylamine hydrochloride. The platinichloride was prepared, recrystallised, and analysed.

0·0878 yielded on ignition 0·0326 Pt. Pt = 37·1.

$(NH_2 \cdot C_3H_7)_2,H_2PtCl_6$ requires Pt = 37·0 per cent.

The action of propyl iodide on this oxime is therefore analogous to that of ethyl iodide.

Action of Methyl Iodide on Acetaldoxime in the presence of Sodium Methoxide. Methylacetaldoxime and Methylisoacetaldoxime.

When methyl iodide is added to a solution of acetaldoxime and sodium methoxide in methyl alcohol, a vigorous reaction takes place, requiring the flask to be kept well cooled. The method adopted was to cool the solution of acetaldoxime and sodium methoxide to 0°, and gradually to add the methyl iodide through the upright condenser tube. After the mixture has been kept at 0° for 3 or 4 hours, the temperature is allowed to rise slowly, and the solution finally heated for 15 minutes on the water-bath.

On distillation, the true ether, methylacetaldoxime, passed over in the first fraction; this was treated with calcium chloride and allowed to stand in order to remove the methyl alcohol, the ether distilled off, and again treated with calcium chloride. The pure substance boils at 47·5°. It possesses a sweet, ethereal odour, is soluble in water, and readily miscible with ether and alcohol. A yield of about 10—11 per cent. was obtained. When hydrolysed by heating on the water-bath with hydrochloric acid (5 per cent.), it yields acetaldehyde and α-methylhydroxylamine; the latter was identified by means of its hydrochloride, which melted at 148°, and possessed the general characters of this salt,

$$CH_3\cdot CH{:}N\cdot OCH_3 + H_2O = CH_3\cdot CHO + NH_2\cdot OCH_3.$$

The solution from which the ether had been distilled was transferred to a dish, and concentrated in a vacuous desiccator. A mass of long needles separated; these were drained from the mother liquor, and dried on a porous tile in the desiccator. The substance was recrystallised from warm methyl alcohol, and obtained in long, silky needles. A number of analyses were made, which show that the substance is a compound of methyl*iso*acetaldoxime with sodium iodide, of the composition $(CH_3\cdot CH{-}N\cdot CH_3)_2,NaI$.
$\quad\quad\quad

it yields acetaldehyde and methylamine, which was identified by means of its platinichloride, $CH_3\cdot CH{-}N\cdot CH_3 + H_2 = CH_3\cdot CHO + NH_2\cdot CH_3$.
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Action of Propyl Iodide on Acetaldoxime. Propylacetaldoxime and Propylisoacetaldoxime.

When a solution of acetaldoxime and sodium methoxide in methyl alcohol is treated with propyl iodide, sufficient heat is evolved to produce ebullition; the mixture is afterwards heated for half-an-hour on the water-bath.

On distilling the product, methyl alcohol passes over and carries with it the *propyl ether* of the oxime, which is separated by the addition of water, and after its removal a further quantity is obtained by extracting with ether and drying and distilling the ethereal solution. This ether is a colourless oil, of sweet ethereal odour, and boils at 101—102°; it is almost insoluble in water, but readily dissolves in alcohol and in ether. The yield slightly exceeded 20 per cent. On heating the ether with hydrochloric acid, acetaldehyde and ammonium chloride were produced.

As in the preceding case, the compound of the derivative of the *iso*oxime with sodium iodide could only be obtained as a thick, uncrystallisable liquid. On hydrolysis, it yielded acetaldehyde and a β-hydroxylamine which powerfully reduced a solution of copper sulphate in the cold. When reduced with zinc dust and dilute hydrochloric acid, propylamine was produced and identified by means of its platinichloride. On ignition:

0·0985 gave 0·0363 Pt. Pt = 36·9

$(NH_2 \cdot C_3H_7)_2,H_2PtCl_6$ requires Pt = 37·0 per cent.

There can, therefore, be no doubt that the propyl*iso*oxime is represented by the formula $CH_3 \cdot CH{-}N \cdot C_3H_7$ (O), and the hydrolysis by the equation $CH_3 \cdot CH{-}N \cdot C_3H_7$ (O) $+ H_2O = CH_3 \cdot CHO + NH(C_3H_7) \cdot OH$.

Action of Methyl Iodide on Acetophenoxime in the presence of Sodium Methoxide. Methylacetophenoxime and Methylisoacetophenoxime.

When a solution of acetophenoxime in methyl alcohol is mixed with the calculated quantities of sodium methoxide and methyl iodide, so much heat is developed that the solution boils spontaneously. It is afterwards heated for an hour on the water-bath. After the greater part of the methyl alcohol has been removed by distillation, on the addition of water, the *methyl ether* of acetophenoxime separates as an oil, and is extracted with ether; the ethereal solution is dried with calcium chloride, and the ether carefully distilled off. The compound, $C_6H_5(CH_3)C{:}N \cdot OCH_3$, boils at 214—216° with slight decomposition;

it has a pleasant aromatic odour and is easily soluble in alcohol and ether, but is insoluble in water. The yield was larger than in the cases previously described, probably amounting to as much as 40 per cent.

If the aqueous solution from which the methyl ether has been extracted is distilled, some of the isomeric methyl*iso*oxime suffers hydrolysis, and acetophenone and β-methylhydroxylamine pass over with the steam; the former was identified by conversion into its oxime, melting at 59°, and the latter by means of its deliquescent hydrochloride melting at 80—85°. The *methyl*iso*acetophenoxime* crystallises with sodium iodide to form the compound, $C_6H_5(CH_3)C(O)N\cdot CH_3,NaI$, which is obtained in needles and possesses the usual properties of these substances. On analysis:

0·2040 gave 0·00924 N. N = 4·5.

$C_6H_5(CH_3)C(O)N\cdot CH_3,NaI$ requires N = 4·7 per cent.

On reduction, the methyl*iso*oxime furnishes methylamine. The platinichloride was prepared and analysed.

0·0508 gave 0·0210 Pt. Pt = 41·3.

$(NH_2\cdot CH_3)_2,H_2PtCl_6$ requires Pt = 41·4 per cent.

*Action of Ethyl Iodide on Acetophenoxime. Ethylacetophenoxime and Ethyl*iso*acetophenoxime.*

Ethyl iodide reacts with acetophenoxime in the presence of sodium methoxide in the same manner as methyl iodide.

The *ethyl ether*, $C_6H_5(CH_3)C{:}N\cdot OC_2H_5$, distils at 130—135° under 20 mm. pressure, and boils with some decomposition at 220—225° under ordinary pressure. The yield is approximately 60 per cent. It closely resembles the corresponding methyl ether in its general properties. This ether has been previously described by Trapesonzjanz (*Ber.*, 1893, **26**, 1427), who records its boiling point as 200—202° under 43 mm. pressure.

*Ethyl*iso*acetophenoxime* is obtained as the sodium iodide compound, $C_6H_5(CH_3)C(O)N\cdot C_2H_5,NaI$; it is easily hydrolysed with production of acetophenone and β-ethylhydroxylamine. The latter was obtained as the uncrystallisable hydrochloride, and on reduction yielded ethylamine, which was identified by means of its platinichloride.

0·0870 gave 0·0340 Pt. Pt = 39·1.

Calculated for $(NH_2\cdot C_2H_5)_2,H_2PtCl_6$, Pt = 39·0 per cent.

The methyl and ethyl acetophenoximes and the methyl and ethyl *iso*acetophenoximes therefore resemble the corresponding derivatives of the aliphatic oximes which we have described above.

Direct Reduction of Alkylated iso*Oximes. Formation of Secondary Amines.*

On account of the ease with which the substituted *iso*oximes suffer hydrolysis, it seemed probable that the substances obtained on reduction in presence of water may not be derived directly from the *iso*oximes themselves, but rather from their hydrolytic products; thus, reduction with zinc and dilute acids, with hydriodic acid, or with zinc dust and water always results in the formation of the aldehyde or ketone and of a primary amine furnished by the previously formed β-hydroxylamine. It seemed possible, however, that if the alkylated *iso*oxime itself could be reduced, the oxygen atom might be removed and the corresponding secondary amine formed by direct reduction. Methyl*iso*acetaldoxime, for example, yields under ordinary conditions *methyl-β-hydroxylamine* (or methylamine) and acetaldehyde. If, however, water were excluded, the alkyl *iso*oxime might be converted by reduction into the corresponding secondary amine,

$$CH_3\cdot CH{-}N\cdot CH_3 + 2H_2 = CH_3\cdot CH_2\cdot NH\cdot CH_3 + H_2O.$$
$$\qquad\quad\backslash O/$$

After a great many experiments, the proper condition for the direct reduction of the alkylated *iso*oximes has been found, and by this means a satisfactory confirmation of their constitution has been obtained, and a new method furnished for the preparation of secondary amines, some of which have been hitherto found difficult to prepare in a pure state.

*Direct Reduction of Methyl*iso*acetaldoxime.*

Two grams of the sodium iodide compound of methyl*iso*acetaldoxime were dissolved in 20 c.c. of dry ethyl alcohol and sodium amalgam ($2\frac{1}{2}$ per cent.) was added gradually; the solution was kept acid by the addition of small quantities of glacial acetic acid from time to time, in accordance with the directions given by Goldschmidt (*Ber.*, 1886, 19, 3232). The mixture became warm and the reduction proceeded without the aid of external heat. The bases produced were liberated with sodium hydroxide and distilled into hydrochloric acid; on evaporation, a residue was obtained which was completely soluble in alcohol. The greater part dissolved in chloroform, leaving a small quantity of methylamine hydrochloride. The solution in chloroform yielded, on evaporation, a hygroscopic, crystalline hydrochloride, the platinichloride of which crystallised in long, well-defined, hexagonal prisms melting with decomposition at 202—204°. On analysis:

0·1447 gave 0·0534 Pt. Pt = 36·9.

$(CH_3{\cdot}NH{\cdot}C_2H_5)_2,H_2PtCl_6$ requires Pt = 37·0 per cent.

The aurichloride was also prepared; it crystallised from water in long, slender needles melting at 179—180°.

0·1609 gave 0·0794 Au. Au = 49·3.

$CH_3{\cdot}NH{\cdot}C_2H_5,HAuCl_4$ requires Au = 49·4 per cent.

The characters of these salts agree closely with those of the salts of methylethylamine described by Skraup and Wiegmann (*Monatsh.*, 1889, 10, 110). The methyl*iso*acetaldoxime has therefore been reduced in accordance with the following equation.

$$CH_3{\cdot}CH{-}N{\cdot}CH_3 + 2H_2 = CH_3{\cdot}CH_2{\cdot}NH{\cdot}CH_3 + H_2O.$$
$$\quad\quad\quad

The *picrate* of methyl*iso*propylamine crystallises from hot water in long, pale yellow needles and melts at 133—134°.

The reduction is therefore represented by the equation :

$$(CH_3)_2C\overset{O}{\diagdown\!\diagup}N\cdot CH_3 + 2H_2 = (CH_3)_2CH\cdot NH\cdot CH_3 + H_2O.$$

Reduction of methyl*iso*acetaldoxime and of methyl*iso*acetoxime has also been attempted by means of zinc dust and glacial acetic acid in alcoholic solution under conditions similar to those observed in the reduction with sodium amalgam, but with less satisfactory results. Methyl*iso*acetaldoxime furnished approximately equal quantities of the hydrochlorides of methylamine and methylethylamine, the latter being identified by means of its aurichloride, which after recrystallisation melted at 177—178°. Methyl*iso*acetoxime, however, yielded methylamine only and no methyl*iso*propylamine.

The reduction of alkylated *iso*oximes with sodium amalgam may be useful as a general method of obtaining secondary amines.

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LXVI.—*The Supposed Existence of Two Isomeric Triethyloxamines.*

By Wyndham R. Dunstan and Ernest Goulding.

In a previous paper on the "Action of Alkyl Haloids on Hydroxylamine" (Trans., 1899, 75, 792), we showed that by the action of ethyl iodide on an ethereal solution of diethylhydroxylamine a salt of triethyloxamine, $(C_2H_5)_3NO$, is produced. We obtained this base in a crystalline state and gave an account of its properties and those of its principal salts, and showed by the study of its reactions that it was to be regarded as a true oxamine, $(C_2H_5)_3N{:}O$, and not as the isomeric triethylhydroxylamine, $(C_2H_5)_2N\cdot OC_2H_5$. Later (Trans., 1899, 75, 1006), we obtained the same compound by the direct oxidation of triethylamine with hydrogen peroxide.

We also proved that this triethyloxamine is not identical with the compound which Bewad (*J. Russ. Phys. Chem. Soc.*, 1888, 20, 125) had obtained by acting on nitroethane with zinc ethyl. Bewad regarded this substance as the isomeride of a true triethylhydroxylamine and assigned to it the formula $(C_2H_5)_3NO$, on account of its having apparently furnished triethylamine on reduction. As the properties of this compound differed so markedly from ours, it seemed

possible that Bewad had obtained the isomeric triethylhydroxylamine which we had been unsuccessful in producing by any method we had tried. The properties of the substance described by Bewad were, however, not such as would be expected from a substituted hydroxylamine of the formula $(C_2H_5)_2N{\cdot}OC_2H_5$. As the question was one of some theoretical importance, we prepared a quantity of Bewad's material. In the meantime, however, Lachman (*Ber.*, 1900, **33**, 1022) published an account of an investigation of this question. He prepared β-diethylhydroxylamine by the action of zinc ethyl on diphenylnitrosamine. The properties of the substance obtained by this method agree with those of the compound prepared by us by acting on hydroxylamine with ethyl iodide. Having been struck by the remarkable isomerism which apparently existed between the triethyloxamine prepared by us and that obtained by Bewad, Lachman proceeded to compare their properties.

In general, Lachman's account of the properties of triethyloxamine correspond with ours. He has, however, been unsuccessful in crystallising the base and is inclined to regard the crystallisation we observed as due to an impurity. This, however, is a mistake, for we have satisfied ourselves of the purity of the crystalline substance described in our previous paper. If the concentrated aqueous solution of the pure base is left in a vacuous desiccator with phosphoric oxide, it gradually becomes crystalline. These crystals are extremely hygroscopic.

After an examination of the properties of Bewad's compound, Lachman confirms our conclusion that the two substances are not identical and leaves to us the further determination of the question, but we now need only refer to it briefly, since Bewad (*J. Russ. Phys. Chem. Soc.*, 1900, **32**, 455) has shown that his supposed triethylhydroxylamine is really β-ethyl-*sec*-butylhydroxylamine,

$$C_2H_5(CH_3)CH{\cdot}N(C_2H_5){\cdot}OH,$$

which satisfactorily accounts for its properties. Bewad concludes that the action of zinc alkyls on primary or secondary nitroparaffins always results in the formation of β-disubstituted hydroxylamines.

Although Bewad himself does not discuss the supposed isomerism, any further investigation of the matter by us is unnecessary, for the conclusion reached by Bewad is entirely in accordance with our own, but we may point out that the additive compound, which Lachman describes as resulting from the action of methyl iodide on Bewad's compound, cannot possess the constitution or undergo the reactions which he attributes to it. Instead of being represented by the formula $(C_2H_5)_3N(OCH_3)I$, it is probably a hydriodide of methylethyl-*sec*-butyloxamine,

$$CH_3(C_2H_5)(C_4H_9)N{:}O,HI.$$

This being the case, it is clear that it could not undergo the decompositions described by Lachman into formaldehyde and triethylamine and other products.

Bewad has also shown (*loc. cit.*) that β-diethylhydroxylamine results from the action of zinc ethyl on *iso*propyl or *iso*amyl nitrite, and that β-dipropylhydroxylamine may be obtained by the action of zinc propyl on propyl nitrite. These compounds are identical with those we have prepared by the action of ethyl and propyl iodides on hydroxylamine.

We take this opportunity of replying to the complaint made by Mamlock and Wolffenstein (*Ber.*, 1900, **33**, 159) that we have worked on the action of hydrogen peroxide on aliphatic amines, although Wolffenstein had previously stated that he was engaged in the study of the action of hydrogen peroxide on organic bases. Wolffenstein previously had taken similar exception to the work of Bamberger and Tschirner (*Ber.*, 1899, **32**, 342). In the paper referred to above, these authors proceed to describe the properties of β-dipropylhydroxylamine and tripropyloxamine without any allusion to the fact that these compounds have already been prepared by us. As a matter of fact, we commenced the investigation of the action of alkyl haloids on hydroxylamine so long ago as 1894 (Proc., 1894, **10**, 138), and in 1899 (Trans., 1899, **75**, 792; Proc., 1899, **15**, 58) showed that the reaction previously described was a general one by means of which, not only trimethyl, but other alkylated oxamines and hydroxylamines could be prepared. In this paper, we stated that we were attempting to produce these new compounds by the action of hydrogen peroxide on the amines in order to settle their constitution. When Wolffenstein, whose previous investigations had been restricted to the oxidation of pyridine and quinoline derivatives—in which field Merling (*Ber.*, 1892, **25**, 3123) had also worked—announced that he intended to extend his work to the aliphatic amines, our experiments were nearly completed.

In any case, our study of the action of hydrogen peroxide on certain aliphatic amines was undertaken merely to confirm the constitution of the oxides of the amines (oxamines) which we had already prepared by an entirely distinct reaction.

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LXVII.—*Studies in the Camphane Series. Part II. Nitrocamphene, Aminocamphene, and Hydroxycamphene.*

By Martin Onslow Forster.

Among the changes which 1 : 1-bromonitrocamphane is capable of undergoing, not the least interesting is that which involves the removal of hydrogen bromide. By this means there is produced an unsaturated nitro-compound, which, in accordance with the suggestion made in a previous paper (Trans., 1900, 77, 251), will be called 1-*nitrocamphene*.



1 : 1-Bromonitrocamphane. 1-Nitrocamphene.

The noteworthy point in a study of this compound is the fact that its production lays open a way to hydroxycamphene, the enolic modification of camphor, and the present communication gives an account of the steps by which hydroxycamphene has been obtained.

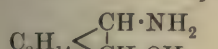
Owing to the susceptibility of camphene to the action of oxidising agents, nitro-derivatives of this hydrocarbon have been hitherto unknown, the nearest approach to compounds of that type being camphene nitronitrosite, $C_8H_{14}<\begin{matrix}C(NO)\cdot NO_2\\ |\\ CH\cdot NO_2\end{matrix}$, and camphene nitrosite,

$$C_8H_{14}<\begin{matrix}CH\cdot NO\\ |\\ CH\cdot NO_2\end{matrix},$$

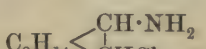
obtained by Jagelki from camphene and nitrous acid (*Ber.*, 1899, 32, 1498). These, however, being saturated, are not genuine camphene derivatives, but belong rather to the camphane series. The first representative of the nitrocamphenes has been prepared by heating an alcoholic solution of 1 : 1-bromonitrocamphane with silver nitrate. Although melting at 56°, the substance displays extraordinary readiness to crystallise; it is an unsaturated compound, yielding additive derivatives with bromine, hydrogen iodide, and hydrogen bromide. As might be anticipated, the last-named gives rise to a bromonitrocamphane which is distinct from 1 : 1-bromonitrocamphane, and as it yields neither camphoroxime nor bornylamine on reduction, must have the constitution of a 2-bromo-1-nitrocamphane, $C_8H_{14}<\begin{matrix}CHBr\\ |\\ CH\cdot NO_2\end{matrix}$.

When 1-nitrocamphene is heated with zinc dust and glacial acetic acid, the nitro-group alone is reduced, and the unsaturated link remaining unaltered, 1-*aminocamphene* is obtained. This base is not the first of the aminocamphenes. Duden and Macintyre (*Annalen*, 1900,

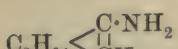
313, 59) have recently prepared 2-aminocamphene, or camphenamine; through the agency of phosphorus pentachloride, they replaced the hydroxyl in aminoborneol by chlorine, and obtained camphenamine from the product by the action of caustic soda.



Aminoborneol. (1-Hydroxy-2-amino-camphane.)

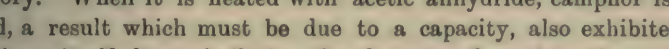


Chlorocamphanamine. (1-Chloro-2-amino-camphane.)



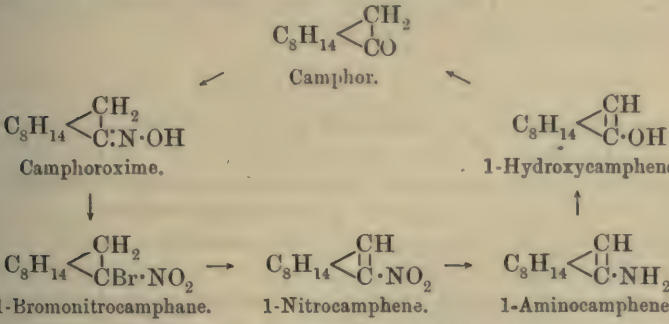
Camphenamine. (2-Aminocamphene.)

1-Aminocamphene is quite distinct from camphenamine. It is a translucent solid which melts at 46° and boils at 191—192° under atmospheric pressure; unlike the isomeride, it is strongly dextrorotatory. When it is heated with acetic anhydride, camphor is produced, a result which must be due to a capacity, also exhibited by camphene itself, for assimilating the elements of acetic acid:



The chief interest attaching to 1-aminocamphene is due to its conversion into 1-*hydroxycamphene* under the influence of nitrous acid. When the sulphate of the base, dissolved in water, is heated with potassium nitrite, nitrogen is liberated, and the hydroxy-compound is produced. The substance crystallises in long needles, has a faint, camphor-like odour, and melts at 74°; although indifferent towards alkalis, warm dilute mineral acids convert it immediately into ordinary camphor yielding an oxime of normal rotatory power.

The complete cycle of changes by which camphor has been converted into the tautomeric hydroxy-compound and then regenerated from the latter is represented by the following formulæ:



Hydroxycamphene is an unexpectedly stable substance, and shows no tendency to change into camphor excepting under the influence of acids. It may be distilled under atmospheric pressure without suffer-

ing alteration, and, unlike the enolic modifications of diketones or of ketonic esters, is quite indifferent towards ferric chloride.

In view of these peculiarities, the substance and its derivatives are being subjected to further investigation.

Experimental.

1-*Nitrocamphene*, $C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot NO_2\end{matrix}$.

One hundred grams of 1 : 1-bromonitrocamphane were dissolved in 1000 c.c. of absolute alcohol and heated in a reflux apparatus with 110 grams of powdered silver nitrate, which was added in quantities of 10 grams at intervals of about 2 hours. Twice before the operation was complete the liquid was filtered from silver bromide, and when the clear solution no longer became turbid on being heated alone, alcohol was boiled off by means of a water-bath. The viscous oil remaining in the flask was then distilled in a current of steam, yielding a colourless, crystalline substance which was readily fusible, and very volatile in steam. The product was filtered, drained on porous earthenware, and treated with a very small quantity of cold alcohol, in which the crude material was freely soluble; the alcohol removed an oily bye-product, and when the solid had been filtered from this, it became safe to dissolve it in a small quantity of hot alcohol, from which it crystallised readily on cooling. The yield of nitrocamphene is disappointing, and is liable to wide fluctuations if the foregoing process is not followed closely, but under favourable circumstances 35 grams of the recrystallised nitro-derivative may be obtained from 100 grams of bromonitrocamphane, scarcely more than 50 per cent. of the theoretical amount.

It will be noticed that the quantity of silver nitrate employed in the preparation of nitrocamphene considerably exceeds the amount required by the equation

$$C_{10}H_{16}Br\cdot NO_2 + AgNO_3 = C_{10}H_{15}\cdot NO_2 + AgBr + HNO_3;$$

it approaches, indeed, two molecular proportions, but experiment has shown that a result of using smaller quantities is the contamination of the product with unchanged bromonitrocamphane. Doubtless the excess of silver nitrate in part explains the diminution in yield, as it probably exerts an oxidising action. The same effect is of course produced by the nitric acid set free; the latter is largely appropriated by the alcohol, which becomes converted into ethyl nitrite, but as 100 grams of bromonitrocamphane liberate 24 grams of nitric acid, a considerable portion of the product must suffer oxidation. An attempt has been made to overcome this difficulty by the employment of silver oxide or silver acetate, but neither of these substances lends itself to

the removal of hydrogen bromide from bromonitrocamphane; both, it is true, are converted into silver bromide, but the change is so slow, and so far from complete, as to offer no hope of economising silver by this modification of the process. Another reason for the large excess of silver nitrate required in practice is revealed by the fact that a certain amount leaves the solution without precipitating the bromide, but merely combined with that salt. In the earlier experiments, it was customary to add the silver nitrate in quantities of 20—30 grams, until it was noticed that the precipitate differed from silver bromide in appearance; on examination, it proved to consist of the molecular compound of silver bromide with silver nitrate.

Nitrocamphene dissolves readily in hot alcohol, crystallising in long, hard, striated prisms resembling α-bromocamphor; it melts at 56°, and boils under atmospheric pressure without undergoing alteration, but although so readily fusible, its tendency to crystallise is unusually pronounced. On analysis:

0·1517 gave 0·3702 CO_2 and 0·1130 H_2O. C = 66·55; H = 8·28.
$C_{10}H_{15}O_2N$ requires C = 66·29; H = 8·28 per cent.

It is quite colourless, and has a faint odour which becomes very intense when the vapour is carried off with steam, then resembling that of 1 : 1-bromonitrocamphane; the substance is insoluble in water, but dissolves very readily in cold benzene, petroleum, chloroform, or ethyl acetate. It gives Liebermann's reaction for nitroso-derivatives.

A solution containing 0·5062 gram of nitrocamphene in 25 c.c. of absolute alcohol at 21° gave α_D +4°32′ in a 2 dcm. tube, whence the specific rotatory power $[\alpha]_D$ +112·0°; 1 gram dissolved in 25 c.c. of benzene at 21° gave α_D +11°0′ in the same tube, corresponding to $[\alpha]_D$ +137·5°.

Nitrocamphene undergoes no change when treated with boiling acetic anhydride in a reflux apparatus during several hours.

2-*Bromo*-1-*nitrocamphane*, $C_8H_{14}<\begin{matrix}CHBr\\ |\\ CH\cdot NO_2\end{matrix}$.

Twenty c.c. of fuming hydrobromic acid (sp. gr. 1·83) were placed in a large, wide mouthed weighing bottle, and 5 grams of finely powdered nitrocamphene were quickly added to the liquid, which was stirred thoroughly during the operation. No rise of temperature took place, but the suspended solid soon hardened and became compact. After a couple of hours, during which the substance was thoroughly incorporated with the acid, a considerable quantity of water was added, and the filtered product was washed several times.

2-Bromo-1-nitrocamphane crystallises from alcohol in fern-like

aggregates of white needles, and melts at 178° to a colourless liquid which evolves gas. On analysis:

0·1875 gave 0·1368 AgBr. Br = 31·05.

$C_{10}H_{16}O_2NBr$ requires Br = 30·53 per cent.

In appearance the substance closely resembles 1 : 1-bromonitrocamphane, forming a tough, camphor-like mass when compressed; its odour, however, is scarcely perceptible, and it does not distil at all readily in steam. It gives Liebermann's reaction, and the alcoholic solution immediately yields a precipitate of silver bromide when warmed with silver nitrate.

A solution containing 0·5089 gram dissolved in 25 c.c. of benzene at 21° gave α_D +9′ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D$ +3·7°.

The behaviour of 2-bromo-1-nitrocamphane towards concentrated sulphuric acid at once differentiates it from the isomeride; whilst the latter loses the elements of water, and gives rise to the anhydride, $C_{10}H_{14}ONBr$ (Trans., 1899, 75, 1141), the new derivative merely dissolves in the acid, from which it is precipitated on dilution with water.

1 : 2-*Dibromo*-1-*nitrocamphane*, $C_8H_{14}<\begin{matrix}CHBr\\ |\\ CBr\cdot NO_2\end{matrix}$.

When a solution of bromine in chloroform is added to nitrocamphene in the same solvent, the colour of the halogen persists, but if left in contact with the nitro-derivative during several hours, the bromine is gradually absorbed.

Five grams of nitrocamphene were dissolved in dry chloroform and cooled by immersion in melting ice; 4·5 grams of bromine dissolved in 20 c.c. of the solvent were then added, and the mixture allowed to remain in a stoppered bottle during 24 hours. The crystalline residue obtained on evaporating the chloroform was drained on porous earthenware and recrystallised twice from alcohol, which deposited long, flat, transparent needles melting at 195° to a colourless liquid evolving gas. On analysis:

0·1388 gave 0·1523 AgBr. Br = 46·69.

$C_{10}H_{15}O_2NBr_2$ requires Br = 46·91 per cent.

Dibromonitrocamphane dissolves very readily in cold chloroform, benzene, or ethyl acetate, but is only sparingly soluble in hot petroleum or cold alcohol; it gives Liebermann's reaction, but much less readily than the mono-halogen derivatives of nitrocamphane, requiring to be heated with the acid during a longer period than usual.

A solution containing 0·4942 gram dissolved in 25 c.c. of benzene at 19° gave α_D +10′ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D$ +4·2°.

2-Iodo-1-nitrocamphane, $C_8H_{14}<\begin{matrix}CHI\\|\\CH\cdot NO_2\end{matrix}$.

When left in contact with fuming hydriodic acid (sp. gr. 1·94) during 2 hours, nitrocamphene becomes completely converted into 2-iodo-1-nitrocamphane. This compound, after being washed thoroughly with water and twice crystallised from the minimum quantity of hot alcohol, forms lustrous, thin plates, which begin to darken at 100°, and melt to a deep brown liquid at 118°. On analysis:

0·2019 gave 0·1507 AgI. I = 40·33.

$C_{10}H_{16}O_2NI$ requires I = 41·10 per cent.

The compound is quite distinct from 1 : 1-iodonitrocamphane in appearance, but is quite as unstable; solutions of the substance in organic media spontaneously undergo change, a solution in benzene, for instance, becoming violet after an interval of a few hours. It is readily soluble in benzene and in ethyl acetate, being more sparingly soluble in alcohol; it is important to recrystallise the substance as quickly as possible in order to avoid loss. It gives Liebermann's reaction for nitroso-derivatives.

A solution containing 0·3557 gram dissolved in 25 c.c. of absolute alcohol at 20° gave α_D −1°0′ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D$ −35·1°; 0·3676 gram dissolved in 25 c.c. of benzene at 18° gave α_D −52′ in the same tube, corresponding to $[\alpha]_D$ −29·4°.

1-Aminocamphene, $C_8H_{14}<\begin{matrix}CH\\\|\\C\cdot NH_2\end{matrix}$.

Twenty-five grams of recrystallised nitrocamphene were dissolved in 250 c.c. of glacial acetic acid to which 50 grams of zinc dust were then added. After remaining surrounded with cold water during 1 hour, the liquid was heated in boiling water during 2 hours, filtered from zinc, diluted with water, evaporated on the water-bath, and finally submitted to a current of steam, which carried over a small quantity of unaltered nitrocamphene. A concentrated solution of 75 grams of caustic soda in water was then added to the liquid, and the oil which rose to the surface was distilled in a current of steam. The base being somewhat soluble in cold water, concentrated potash was added to the aqueous distillate, which was then extracted with ether the solution was dried with solid potash, and evaporated, the residue being distilled under the ordinary pressure.

1-Aminocamphene is a translucent solid closely resembling camphene in appearance. It melts at 46°, and boils at 191—192° under 758 mm. pressure; the odour resembles that of bornylamine, but is more distinctly ammoniacal. On analysis:

0·1773 gave 0·5179 CO_2 and 0·1767 H_2O. C = 79·55; H = 11·07.
$C_{10}H_{17}N$ requires C = 79·47; H = 11·25 per cent.

A solution containing 0·4453 gram dissolved in 25 c.c. of absolute alcohol at 22°, gave α_D +2° 7·5′ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D$ +59·7°; 0·4803 gram dissolved in 25 c.c. of benzene at 22° gave α_D +1°40′ in the same tube, corresponding to $[\alpha]_D$ +43·4°.

The base is strongly alkaline towards litmus, and does not reduce an ammoniacal solution of silver nitrate; it instantaneously decolorises a solution of bromine in chloroform, and rapidly reduces a neutral solution of potassium permanganate.

The *sulphate* dissolves readily in water, from which it crystallises in lustrous leaflets which melt and evolve gas at 256°.

The *platinichloride* dissolves very readily in alcohol, and crystallises slowly in large, transparent, six-sided plates, pale red in colour; it melts and decomposes at 243°.

0·3300 gave 0·0879 Pt. Pt = 26·64.
$(C_{10}H_{17}N)_2,H_2PtCl_6$ requires Pt = 27·32 per cent.
$(C_{10}H_{17}N)_2,H_2PtCl_6 + H_2O$ „ Pt = 26·65 „

The *benzoyl* derivative, easily prepared by the Schotten-Baumann method, is readily soluble in benzene, chloroform, or alcohol, but only sparingly so in petroleum; it crystallises from the last named solvent in white, silky needles melting at 157°.

0·1721 gave 0·5032 CO_2 and 0·1266 H_2O. C = 79·73; H = 8·17.
$C_{17}H_{21}ON$ requires C = 80·00; H = 8·23 per cent.

The substance behaves as an unsaturated compound towards bromine, which it decolorises immediately. A solution containing 0·3701 gram dissolved in 25 c.c. of absolute alcohol at 18°, gave α_D +55′ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D$ +30·9°.

The *benzylidene* derivative is produced immediately on mixing the fused base with benzaldehyde, when water separates, and the viscous liquid rapidly solidifies. It is purified by melting it with a small quantity of alcohol, draining on porous earthenware the crystals obtained on cooling the liquid, and recrystallising the product from hot alcohol, which deposits it in transparent, six-sided plates melting at 63°.

0·1630 gave 0·5137 CO_2 and 0·1297 H_2O. C = 85·95; H = 8·84.
$C_{17}H_{21}N$ requires C = 85·35; H = 8·79 per cent.

The *picrate* crystallises rapidly on mixing alcoholic solutions of picric acid and the base. It is sparingly soluble in cold alcohol, but dissolves readily in the hot liquid, from which it separates in lustrous, canary-yellow needles. The salt melts to a brown liquid at 231°, and immediately evolves gas.

0·1032 gave 13·1 c.c. nitrogen at 15·5° and 753 mm. N = 14·73.
$C_{16}H_{20}O_7N_4$ requires N = 14·73 per cent.

The *phenylcarbamide* is at once produced on mixing ethereal solutions of the base and phenylcarbimide in molecular proportion. It crystallises from boiling alcohol in lustrous, white needles and melts at 213°.

0·1546 gave 0·4285 CO_2 and 0·1158 H_2O. C = 75·57; H = 8·32.
$C_{17}H_{22}ON_2$ requires C = 75·55; H = 8·15 per cent.

Action of Acetic Anhydride on 1-*Aminocamphene.*—With the object of preparing an acetyl derivative, the base was heated with glacial acetic acid and acetic anhydride in a reflux apparatus during 8 hours, the liquid being then poured into water. After several days the precipitated oil solidified, and was found to dissolve freely in light petroleum, from which it crystallised in lustrous plates melting at 79°. When the acetic acid filtrate from this substance was exactly neutralised with potash and distilled in a current of steam, a considerable proportion of camphor was obtained; this yielded an oxime of which the melting point and specific rotatory power were identical with those of ordinary camphoroxime; the aqueous liquid from which the camphor was distilled yielded ammonia when treated with alkali.

1-*Hydroxycamphene*, $C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot OH\end{matrix}$.

In preparing hydroxycamphene from aminocamphene, advantage was taken of the experience gained by Duden and Macintyre in their attempt to obtain a new camphor from camphenamine (*loc. cit.*).

Twenty-five grams of aminocamphene sulphate were dissolved in 250 c.c. of ice-cold water, and treated with 5·3 grams of potassium nitrite dissolved in the minimum quantity of water. After remaining at the ordinary temperature during 12 hours, no change had taken place, and the liquid was therefore heated on the water-bath during 4 hours in a reflux apparatus; throughout this period, nitrogen was slowly evolved, and an oil separated. This was distilled in a current of steam, and the product, which rapidly crystallised in the condenser, was drained on porous earthenware and dried in the desiccator. Only 6 grams of hydroxycamphene were obtained, but the unaltered base was easily recovered from the residue in the distilling flask by adding alkali.

Hydroxycamphene has a faint odour recalling that of borneol or camphor, and becoming intensified to a pleasant, refreshing perfume when the substance is heated with water. It melts at 74°, and boils at 212° under 750 mm. pressure. It is much too freely soluble in organic media to crystallise easily from these, but when the fused substance is allowed to cool slowly, it solidifies in long, tough, striated needles. Owing to its volatility, some difficulty was experienced in analysing the substance.

0·1425 gave 0·4131 CO_2 and 0·1305 H_2O. C = 79·06 ; H = 10·17.
0·1641 ,, 0·4779 CO_2 ,, 0·1539 H_2O. C = 79·42 ; H = 10·42.
$C_{10}H_{16}O$ requires C = 78·95 ; H = 10·52 per cent.

A solution containing 1·0059 grams, dissolved in 25 c.c. of absolute alcohol at 19°, gave α_D +2°45′ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D$ +34·1° ; 0·53 gram dissolved in 25 c.c. of benzene at 20° gave α_D +1°15′ in the same tube, corresponding to $[\alpha]_D$ +29·5°.

Hydroxycamphene is indifferent towards hydroxylamine and semicarbazide. It reduces cold potassium permanganate freely, although at first the action is slow, owing to the sparing solubility of hydroxycamphene in water ; a solution in chloroform instantly decolorises bromine in the same solvent, but the first few drops only are absorbed, probably because the small quantity of hydrogen bromide produced is sufficient to convert the remaining hydroxycamphene into camphor Contrary to expectation, hydroxycamphene does not develop a red coloration with ethereal or alcoholic solutions of ferric chloride, and is equally indifferent towards copper acetate ; it is quite stable in presence of alkalis, but warm, dilute mineral acids transform it immediately into ordinary camphor.

Action of Sulphuric Acid on Hydroxycamphene.—One gram of hydroxycamphene was dissolved in 10 c.c. of ice-cold sulphuric acid, the solution being poured immediately on crushed ice. The precipitate was collected washed, and heated in alcohol with hydroxylamine hydrochloride and caustic soda ; on evaporating the alcohol, diluting with water, neutralising with dilute sulphuric acid, and recrystallising from petroleum, a specimen of camphoroxime was obtained melting at 119°, and giving $[\alpha]_D$ −40·2° in absolute alcohol.

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LXVIII.—*Studies in the Camphane Series. Part III. Action of Hydroxylamine on the Anhydrides of Bromonitrocamphane.*

By Martin Onslow Forster.

From time to time I have made attempts to elucidate the nature of the change which takes place when 1 : 1-bromonitrocamphane is dissolved in concentrated sulphuric acid. Empirically, the elements of water are withdrawn, but owing to the unusual source of the oxygen, namely, a nitro-group, it is difficult to ascribe a constitutional formula to the product. The latter, moreover, is readily converted into an isomeric compound, yielding a benzoyl derivative, which distinguishes it from the original anhydride (Trans., 1899, **75**, 1141). The relation subsisting between these two substances must be an exceedingly close one not only because they both yield infracampholenonitrile when heated with alkalis, but also because such mild agents as alcoholic ammonia, phenylhydrazine, and hydroxylamine are capable of converting the original anhydride, which has no definite melting point but chars at about 220°, into the unusually well-defined isomeride which melts to a colourless liquid at 240°.

One of the most perplexing features of the inquiry has been the fact that, although it is impossible to suggest a plausible formula which does not contain an unsaturated link, both substances behave towards bromine and potassium permanganate like saturated compounds. In view of the fact that 2-bromo-1-nitrocamphane, $C_8H_{14}<\begin{matrix}CHBr\\ |\\ CH\cdot NO_2\end{matrix}$, merely dissolves in concentrated sulphuric acid without yielding an anhydride, it seems probable that the first step in the change consists in the removal of an atom of oxygen in association with both hydrogen atoms occupying the 2-position.

$$C_8H_{14}<\begin{matrix}CH_2\\ |\\ CBr\cdot NO_2\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}C\\ ||\\ CBr\end{matrix}>NO.$$

It is by no means certain, however, that this takes place, because 1-nitrocamphane, $C_8H_{14}<\begin{matrix}CH_2\\ |\\ CH\cdot NO_2\end{matrix}$, is quite indifferent to concentrated sulphuric acid. Having regard to Wallach's description of the transformation undergone by certain oximes when treated with sulphuric acid (*Annalen*, 1899, **309**, 1 ; 1900, **312**, 171), it seemed possible that the formula $C_8H_{14}<\begin{matrix}CO\\ |\\ CBr\end{matrix}>N$ might apply to one or other of the anhydrides $C_{10}H_{14}ONBr$. I therefore subjected them to the action of

hydroxylamine, and found that both combine with that substance; the product, which is the same in each case, is not the oxime $C_{10}H_{15}ON_2Br$, but a hydroxylamino-derivative, $C_{10}H_{17}O_2N_2Br$. Unfortunately, the investigation of this substance has not thrown much light on the original question, and I can only record a description of its properties.

The compound $C_{10}H_{17}O_2N_2Br$ appears to be a true hydroxylamino-derivative, because it is sufficiently basic to form salts, and reduces ferric chloride and ammoniacal silver nitrate. Nitrous acid regenerates the anhydride melting at 240°, in accordance with the equation

$$C_{10}H_{17}O_2N_2Br + HNO_2 = C_{10}H_{14}ONBr + N_2O + 2H_2O.$$

Oxidation with potassium permanganate in dilute sulphuric acid converts it into a substance, $C_{10}H_{14}O_2NBr$, which is insoluble in dilute acids and alkalis, and which slowly yields infracampholenonitrile when heated with caustic soda.

The most interesting property of the hydroxylamino-derivative is its behaviour towards caustic soda. Whilst the anhydrides yield infracampholenonitrile, $C_9H_{13}N$, when heated with that agent, the compound $C_{10}H_{17}O_2N_2Br$ merely loses the elements of hydrogen bromide and yields another hydroxylamino-derivative, $C_{10}H_{16}O_2N_2$. This substance dissolves readily in acids and alkalis; it is also very sensitive towards oxidising agents, but the product of the action of potassium permanganate has not been isolated, owing to the readiness with which alkalis transform it into infracampholenonitrile.

Experimental.

Hydroxylamino-derivative of Bromonitrocamphane Anhydride, $C_{10}H_{17}O_2N_2Br$.

Fifty grams of the anhydride of bromonitrocamphane were dissolved in 400 c.c. of hot absolute alcohol, the solution being rapidly cooled and treated with 40 grams of anhydrous sodium carbonate; 50 grams of hydroxylamine hydrochloride dissolved in the minimum quantity of hot water were then added, and the mixture, after being allowed to remain at the ordinary temperature until evolution of carbon dioxide had apparently ceased, was heated during 5 hours in a reflux apparatus. Sixteen grams of sodium carbonate followed by 20 grams of hydroxylamine hydrochloride were afterwards added, and the liquid heated in a reflux apparatus during a further period of 5 hours, this treatment being considered necessary because preliminary experiments had shown that a portion of the anhydride is liable to escape conversion into the hydroxylamino-derivative. Alcohol was then distilled off on the water-bath, and the residue poured into its own volume of cold water, the white, crystalline product being collected, washed, and recrystallised twice from hot alcohol.

The compound obtained in this way separates from alcohol in lustrous, transparent, rectangular plates, and melts at 197° to a pale yellow liquid which becomes deep brown in a few minutes, even if the temperature is not raised above 200°. It is practically insoluble in petroleum, and sparingly soluble in ether, but dissolves readily in ethyl acetate, from which it crystallises in tufts of silky needles; it also dissolves in boiling water, and separates in crystals on cooling.

0·1816 gave 0·2905 CO_2 and 0·1033 H_2O. C = 43·62; H = 6·32.
0·2278 ,, 20·6 c.c. nitrogen at 17·5° and 752 mm. N = 10·36.
0·2250 ,, 0·1522 AgBr. Br = 28·78.
$C_{10}H_{17}O_2N_2Br$ requires C = 43·32; H = 6·14; N = 10·11; Br = 28·90 per cent.

The hydroxylamino-derivative is not soluble in cold caustic soda, but dissolves readily in dilute sulphuric acid, from which it is reprecipitated by alkalis; the cold solution in the sulphuric acid decolorises potassium permanganate immediately. Ammoniacal silver nitrate is rapidly reduced when gently warmed with an alcoholic or aqueous solution, and mercuric chloride immediately yields a precipitate of calomel, but the substance is indifferent towards mercury acetamide. Fehling's solution becomes dark green without precipitation of cuprous oxide; a solution in hydrochloric acid is indifferent towards ferric chloride, but when suspended in water alone the substance is immediately dissolved by the agent, which develops a dark red coloration and undergoes reduction in the process. The compound does not answer to Liebermann's test for nitroso-derivatives, and is indifferent towards benzaldehyde, in which it merely dissolves when heated, crystallising very readily from the solution in transparent, rectangular plates. It dissolves sparingly in hot methyl iodide and does not combine with it.

The behaviour of bromonitrocamphane anhydride towards hydroxylamine is another instance of the readiness with which that substance undergoes conversion into the isomeride melting at 240°, for there can be no doubt that this compound is the first product of the action of the base. This is suggested by the circumstance that when the isomeride in question is treated with hydroxylamine under the conditions formulated above, the product is identical in all points with the derivative just described; it is proved by the fact that, on one occasion, when the second treatment with hydroxylamine was omitted, the first alcoholic mother liquor of the product yielded on evaporation a deposit which combined with benzoyl chloride, forming the benzoyl derivative of the anhydride melting at 240°, instead of the benzoyl derivative of the hydroxylamino-derivative, which is described below.

The *hydrochloride* of the hydroxylamino-derivative dissolves readily in hot water, and crystallises in aggregates of minute, white needles;

it begins to darken at about 230°, and melts at 245°, forming a deep brown liquid which immediately effervesces vigorously.

The *sulphate* crystallises from boiling water in lustrous leaflets which soften at about 180° and melt, darken, and evolve gas at 196°.

0·1618 gave 0·0953 AgBr. Br = 25·06.

$(C_{10}H_{17}O_2N_2Br)_2,H_2SO_4$ requires Br = 24·54 per cent.

The *platinichloride* separates in small, pale red crystals on adding aqueous platinic chloride to an alcoholic solution of the substance. It is sparingly soluble in cold alcohol, but dissolves readily on adding hydrochloric acid, crystallising from the solution in minute, pale red needles which melt, char, and evolve gas at 255°.

0·2161 gave 0·0429 Pt. Pt = 19·85.

$(C_{10}H_{17}O_2N_2Br)_2,H_2PtCl_6$ requires Pt = 20·19 per cent.

The *picrate* dissolves readily in alcohol, and crystallises slowly in large, sulphur-yellow rhombohedra, melting to a deep brown liquid which evolves gas at about 190°.

0·1911 gave 0·0685 AgBr. Br = 15·25.

$C_{10}H_{17}O_2N_2Br,C_6H_3O_7N_3$ requires Br = 15·81 per cent.

The *carbamide* derivative is immediately precipitated on adding aqueous potassium cyanate to the hydrochloride of the hydroxylamino-derivative. It is scarcely soluble in cold water, and does not dissolve very freely on boiling; the hot liquid deposits minute, lustrous, flat needles.

0·2303 gave 0·1287 AgBr. Br = 23·77.

$C_{11}H_{18}O_3N_3Br$ requires Br = 23·67 per cent.

The substance softens some degrees before fusion, which takes place at 139° with evolution of gas; it is readily soluble in alcohol, and reduces ammoniacal silver nitrate on boiling.

The *benzoyl* derivative dissolves readily in hot alcohol, and being sparingly soluble in the cold medium crystallises from it in lustrous, transparent prisms.

0·2300 gave 0·1135 AgBr. Br = 21·00.

$C_{17}H_{21}O_3N_2Br$ requires Br = 21·00 per cent.

It becomes brown at 180°, when it melts and evolves gas; it is insoluble in cold dilute sulphuric acid, and does not reduce hot ammoniacal silver nitrate.

The *diacetyl anhydride* is produced when the hydroxylamino-derivative is heated with a mixture of glacial acetic acid and the anhydride in a reflux apparatus. It crystallises very readily from hot

alcohol, separating in transparent, well-formed, hexagonal prisms melting at 139°.

0·2625 gave 0·1434 AgBr. Br = 23·24.

0·2479 „ 0·1354 AgBr. Br = 23·24.

$C_{14}H_{21}O_3N_2Br$ requires Br = 23·19 per cent.

The derivative reduces ammoniacal silver nitrate slowly on continued boiling.

Action of Nitrous Acid on the Hydroxylamino-derivative.

The substance was dissolved in glacial acetic acid, diluted with water, and cooled in melting ice. A small quantity of a concentrated solution of sodium nitrite was added, the first few drops developing a deep yellow coloration; the liquid remained clear during a few seconds, when the colour disappeared, gas was evolved, and a white, crystalline precipitate separated. Further addition of nitrite again developed colour, which was quickly discharged. When the solution remained indifferent to the agent, the precipitate was filtered, washed, and recrystallised twice from hot alcohol.

0·2919 gave 0·2208 AgBr. Br = 33·23.

$C_{10}H_{14}ONBr$ requires Br = 32·79 per cent.

The substance crystallised in transparent, six-sided plates, and melted at 240°, being identical with the compound obtained by the action of hydrochloric acid on the anhydride of bromonitrocamphane (Trans., 1899, **75**, 1146).

Oxidation of the Hydroxylamino-derivative.

Ten grams of the hydroxylamino-derivative were dissolved in 100 c.c. of dilute sulphuric acid (1 : 7), cooled by immersion in melting ice, and oxidised with 250 c.c. of an ice-cold 2 per cent. solution of potassium permanganate. This was added in small quantities at a time, each portion being decolorised before a further amount was added. At first the liquid remained clear, but very soon a white turbidity appeared, rapidly deepening to a distinct precipitate. When the stated amount of permanganate had been added, a further quantity was obtained by treating the filtrate with 80 c.c. of the oxidising agent, which then became reduced only after a long interval. The colourless product, when washed and dried, weighed 9 grams; it was recrystallised twice from alcohol, which deposited a finely-divided, crystalline powder.

0·1670 gave 0·2835 CO_2 and 0·0871 H_2O. C = 46·30; H = 5·80.

0·3187 „ 14·6 c.c. nitrogen at 16° and 755 mm. N = 5·31.

0·2388 „ 0·1720 AgBr. Br = 30·65.

$C_{10}H_{14}O_2NBr$ requires C = 46·15; H = 5·40; N = 5·38; Br = 30·77 per cent.

The substance begins to darken at about 200°, and melts to a deep brown liquid evolving gas at 240°. It dissolves very readily in cold alcohol, forming a solution which is indifferent towards hot ammoniacal silver nitrate. Boiling water dissolves it very sparingly, yielding minute crystals as the solution cools. It is insoluble in caustic soda, and when heated with the alkali slowly gives rise to the nitrile of infracampholenic acid.

Behaviour of the Hydroxylamino-derivative towards Caustic Soda.

Twenty grams of the hydroxylamino-derivative were suspended in 100 c.c. of 15 per cent. aqueous caustic soda and heated, first in boiling water, and finally over a flame until a clear solution was obtained. This occupied scarcely more than one minute, and the pale yellow liquid had only a very faint odour of infracampholenonitrile. The behaviour of the hydroxylamino-derivative towards hot caustic soda is therefore totally different from that of the anhydride of bromonitrocamphane. If allowed to cool slowly, the clear liquid deposited lustrous, white needles, but when rapidly cooled, no separation took place; on adding hydrochloric acid to the cold, clear solution until a permanent turbidity was formed, the liquid contents of the vessel suddenly became semi-solid, from the separation of a snow-white, crystalline precipitate. This was filtered, and the filtrate, which was still alkaline to litmus, exactly neutralised with dilute hydrochloric acid, when it yielded a further quantity of precipitate; the latter, when recrystallised from the minimum quantity of boiling water, weighed 15 grams.

0·2000 gave 0·4491 CO_2 and 0·1446 H_2O. C = 61·24; H = 8·03.
0·2525 ,, 31·3 c.c. nitrogen at 17° and 761 mm. N = 14·40.
$C_{10}H_{16}O_2N_2$ requires C = 61·22; H = 8·16; N = 14·28 per cent.

The substance is very readily soluble in hot alcohol, from which it crystallises in rhomboidal plates. It also dissolves readily in boiling water, separating in lustrous, transparent leaflets which soften at about 170° and melt at 208° to a pale yellow liquid which soon evolves gas and turns brown. The aqueous solution is indifferent towards cold ammoniacal silver nitrate, but when gently heated develops a magnificent mirror. The compound dissolves readily in dilute caustic soda and in dilute mineral acids, the solution in sulphuric acid decolorising potassium permanganate. When mercuric chloride is added to the aqueous solution, a white precipitate is formed, but this disappears on standing, and no calomel is produced when the liquid is boiled. Ferric chloride develops a deep red coloration without being reduced to the ferrous condition; in presence of free hydro-

chloric acid, however, no development of colour takes place, neither does reduction occur. A cold solution of potassium ferricyanide is reduced almost immediately, but mercury acetamide remains unaltered even on boiling. A solution of bromine in chloroform is not decolorised by the substance.

The *platinichloride* is very soluble in cold alcohol and in hot water, crystallising from the latter in nodules of opaque, pale yellow needles.

0·2009 gave 0·0483 Pt. Pt = 24·04.
0·1813 „ 0·0436 Pt. Pt = 24·05.
$(C_{10}H_{16}O_2N_2)_2,H_2PtCl_6$ requires Pt = 24·25 per cent.

The salt has no definite melting point; it suddenly becomes deep red at about 150°, and then rapidly chars.

The *picrate* crystallises in aggregates of lustrous yellow needles.

0·2080 gave 30·7 c.c. nitrogen at 17° and 754 mm. N = 17·00.
$C_{10}H_{16}O_2N_2,C_6H_3O_7N_3$ requires N = 16·47 per cent.

The salt melts and evolves gas at 148°.

Although the compound $C_{10}H_{16}O_2N_2$ is indifferent towards caustic soda, in which it merely dissolves, the benzoyl derivative could not be obtained by the Schotten-Baumann method because of the readiness with which that substance yields infracampholenonitrile under the influence of caustic soda. No definite product was obtained, moreover, by the action of potassium permanganate in dilute sulphuric acid, or by the action of nitrous acid.

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LXIX.—*Contribution to the Chemistry of the Triazoles. 1-Methyl-5-hydroxytriazoles.*

By George Young, Ph.D., and William Henry Oates, late 1851 Exhibition Scholar.

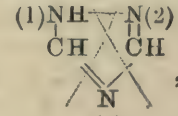
It is to be expected that the possibility of isomerism in the triazole series is similar to that in the pyrazoles, the close relation of the two groups having frequently been pointed out, more especially by Andreocci (*Gazz.*, 1899, 29, ii, 1); the only differences to be foreseen are those produced by the replacement of a methenyl group in pyrazole by an atom of nitrogen in triazole. According to Knorr, isomerism amongst the derivatives of pyrazole is limited by the fact that when position (1) is occupied by a hydrogen atom, positions (3) and (5) are

identical; thus he found that on preparing 3-methylpyrazole, $\begin{matrix}NH\text{—}N\\ |\quad\quad\rangle\\ CH{:}CH\end{matrix}C\cdot CH_3$, and 5-methylpyrazole, $\begin{matrix}NH\cdot N\\ |\quad\quad\rangle\\ CH_3\cdot C{:}CH\end{matrix}CH$, he obtained one substance, instead of two isomerides (*Annalen*, 1894, **279**, 190).

In the triazole series, Young and Witham (Trans., 1900, **77**, 224) endeavoured to prepare a similar pair of isomerides, 3-phenyl-5-hydroxytriazole, $\begin{matrix}NH\cdot N\\ |\quad\quad\rangle\\ OH\cdot C{=}N\end{matrix}C\cdot C_6H_5$, and 5-phenyl-3-hydroxytriazole, $\begin{matrix}NH\cdot N\\ |\quad\quad\rangle\\ C_6H_5\cdot C{=}N\end{matrix}C\cdot OH$. In this case also, one substance, instead of two isomerides, was obtained.

Neither Knorr's results nor those of Young and Witham can, however, be looked upon as definitely deciding the impossibility of such isomerism, as, were both isomerides capable of existence, but with a tendency on the part of either to change into the other, the methods of synthesis used offered most favourable conditions for the occurrence of isomeric change.

The failure to obtain two C-phenylhydroxytriazoles is not surprising if the triazole ring be looked upon as a double amidine, as shown by the dotted lines in the formula



, the two amidine groups, $\cdot C\begin{matrix}N:\\ \diagup\\ \diagdown\\ N\cdot\end{matrix}$, having the nitrogen atom (4) in common. As is well known, all attempts to prepare isomeric amidines of the type $R\cdot C\begin{matrix}NHX\\ \diagup\\ \diagdown\\ NY\end{matrix}$ and $R\cdot C\begin{matrix}NX\\ \diagup\\ \diagdown\\ NHY\end{matrix}$ have resulted in failure (von Pechmann, *Ber.*, 1895, **28**, 869; Wheeler and Johnson, *Ber.*, 1899, **32**, 35).*

According to this view of the triazole ring, the hydrogen atom might wander from position (1) to (4), and from there to position (2), the change thus falling under form C of Lapworth's generalisation (Trans., 1898, **73**, 448), without necessitating the hypothesis of oscillation of the hydrogen atom between two neighbouring nitrogen atoms.

The wandering of the hydrogen atom between positions (1) and (4) is exemplified in the synthesis of triazole by Freund (*Ber.*, 1896, **29**, 2483), who, starting from thiosemicarbazides, obtained derivatives

* The ethenyltriaminonaphthalenes of Markfeldt (*Ber.*, 1898, **31**, 1174) and of Meldola and Eynon (Trans., 1900, **77**, 1159), and the β-phenylaminobenzoxazoles of Kalckhoff (*Ber.*, 1883, **16**, 1826) and of Chelmicki (*J. pr. Chem.*, 1890, [ii], **42**, 440) appear in the literature as isomeric amidines of the above type, but further evidence is required before the structure of these compounds can be considered as proved.

having the formula $\begin{matrix}N\text{——}N\\ \|\\ CR\cdot NR'\end{matrix}\!\!>\!CH$. By this means, he obtained triazole, to which he ascribes the formula $\begin{matrix}N\text{——}N\\ \|\\ CH\cdot NH\end{matrix}\!\!>\!CH$, but found his product to be identical with Andreocci's (*Ber.*, 1892, **25**, 225) and Bladin's (*Ber.*, 1892, **25**, 741) triazole, which, according to the methods of formation used by these authors, has the formula $\begin{matrix}NH\cdot N\\ |\\ CH:N\end{matrix}\!\!>\!CH$.

As all the isomeric pairs of 1 : 3- and 1 : 5-triazole derivatives described in the literature have position (1) occupied by phenyl, we thought it advisable to attempt the preparation of such a pair with methyl in (1) as some guide to the difference which might be expected between the isomerides when (1) is occupied by hydrogen.

The methods which we used were the oxidation of benzal-2-methylsemicarbazone :

$$C_6H_5\cdot CH:N\cdot N(CH_3)\cdot CO\cdot NH_2 \rightarrow \begin{matrix}N\cdot N(CH_3)\\ \|\\ C_6H_5\cdot C\text{——}N\end{matrix}\!\!>\!C\cdot OH,$$

and the oxidation of a mixture of benzaldehyde and von Brüning's methylsemicarbazide (*Annalen*, 1889, **253**, 11), which we expected to take place according to the reaction described by Young (Trans., 1895, **67**, 1063):

$$CH_3\cdot NH\cdot NH\cdot CO\cdot NH_2 + C_6H_5\cdot CHO + O = 2H_2O + \begin{matrix}CH_3\cdot N\cdot N\\ |\quad\|\\ C_6H_5\cdot C:N\end{matrix}\!\!>\!C\cdot OH.$$

To our surprise, both reactions yielded the same product. On investigation, we found the cause of this unexpected result to be that the methylsemicarbazide, made according to von Brüning's directions by the action of potassium cyanate and caustic potash on methylhydrazine sulphate, is 2-methylsemicarbazide, $NH_2\cdot N(CH_3)\cdot CO\cdot NH_2$, and not 1-methylsemicarbazide, as stated by him (*loc. cit.*), as with benzaldehyde it yields the same benzalmethylsemicarbazone as is obtained by reduction of nitrosomethylurea and treatment of the product with benzaldehyde. On heating the phenylmethylhydroxytriazole, obtained by the above reactions, with phosphorus pentasulphide, the methyl group, as well as the hydroxyl, was removed, the product of the reaction being C-phenyltriazole, which we recognised by comparison with a specimen the preparation of which from C-phenylhydroxytriazole will be described in a later paper. This removal of the methyl group by the action of phosphorus pentasulphide agrees with the results obtained by Andreocci (*Atti Real. Accad. Linc.*, 1890, [iv], **6**, ii, 209).

In this paper, we also describe the preparation of other hydroxy-

triazoles by oxidation of methylsemicarbazones, and the preparation of 2-phenyl-1-methyltriazole from 4-methylthiosemicarbazide by the series of reactions described by Marckwald and Bott (*Ber.*, 1896, **29**, 2914).

Experimental.

Benzal-2-methylsemicarbazone, $C_6H_5\cdot CH{:}N\cdot N(CH_3)\cdot CO\cdot NH_2$.

Nitrosomethylurea was reduced with zinc dust and acetic acid in water, according to the instructions given by von Brüning (*loc. cit.*), who made use of this process as an intermediate stage in the preparation of methylhydrazine, but without isolating the resulting methylsemicarbazide or any of its derivatives. Having removed the excess of zinc dust by filtration, we shook the filtrate with benzaldehyde and purified the benzalmethylsemicarbazone, which separated out in a mass of white needles, by recrystallisation from boiling water and from benzene. Benzal-2-methylsemicarbazone is fairly soluble in boiling water, more so in boiling alcohol, benzene, or ethyl acetate, but only slightly so in cold benzene or boiling ether. From the solution in benzene, it can be precipitated by addition of light petroleum. It forms white, delicate needles which melt at 159—160°. When warmed with concentrated hydrochloric acid, it is easily hydrolysed with production of benzaldehyde.

0·1671 gave 0·3743 CO_2 and 0·0946 H_2O. C = 61·09; H = 6·29.
0·2001 „ 40·5 c.c. moist nitrogen at 11·5° and 754 mm. N = 23·88.
$C_9H_{11}ON_3$ requires C = 61·02; H = 6·21; N = 23·73 per cent.

3-Phenyl-1-methylhydroxytriazole, $C_6H_5\cdot C(=N\cdot N(CH_3)\cdot)\!-\!N{>}C\cdot OH$.

Benzalmethylsemicarbazone is easily oxidised by an alcoholic solution of ferric chloride. The action takes place slowly at the ordinary temperature. We obtained the best results by heating the mixture in a closed bottle in boiling water for 1 hour. After removal of the alcohol by a current of steam, the greater part of the product crystallised out on cooling. To recover the remainder from the mother liquor, the iron was precipitated by addition of ammonia, the filtrate from the ferric hydroxide evaporated to dryness, and the residue recrystallised from a mixture of alcohol and ether. The product, on recrystallisation from dilute alcohol, formed long, white, delicate needles which melted at 218—219°.

0·1703 gave 0·3842 CO_2 and 0·0814 H_2O. C = 61·53; H = 5·31.
0·1963 „ 41·1 c.c. moist nitrogen at 15·5° and 753 mm. N = 24·23.
$C_9H_9ON_3$ requires C = 61·71; H = 5·14; N = 24·00 per cent.

This phenylmethylhydroxytriazole is easily soluble in alcohol, fairly so in water, but less so in boiling benzene or ether. It dissolves very easily in alkalis, and is reprecipitated by addition of acids or by boiling the ammoniacal solution, in which case it separates in crystalline flakes. The alkaline solutions do not reduce Fehling's solution or silver nitrate.

On addition of silver nitrate to a slightly ammoniacal solution of the hydroxytriazole, the silver derivative was thrown down as a finely divided, white precipitate, which was dried at 110° until of constant weight.

0·5622 gave 0·2137 Ag. Ag = 38·01.

$C_9H_8ON_3Ag$ requires Ag = 38·30 per cent.

The *acetyl* derivative was prepared by boiling the hydroxytriazole with acetic anhydride and fused sodium acetate. The product was extracted with ether, the ethereal solution washed with dilute aqueous potassium carbonate, dried over calcium chloride, and the ether distilled off. The residue was recrystallised from light petroleum.

The acetyl derivative is easily soluble in alcohol, ether, benzene, or boiling light petroleum. From the last solvent, it crystallises on cooling in beautiful rosettes of white, thin, soft leaflets which melt at 72·5—73°.

0·2103 gave 0·4682 CO_2 and 0·0972 H_2O. C = 60·71 ; H = 5·13.

$C_{11}H_{11}O_2N_3$ requires C = 60·82 ; H = 5·07 per cent.

The acetyl derivative is hydrolysed by boiling with water, yielding phenylmethylhydroxytriazole melting at 218—219°.

Preparation of Phenylmethylhydroxytriazole from Methylhydrazine.

A hot alcoholic solution of ferric chloride (1 mol. Fe_2Cl_6), was added to a boiling alcoholic solution of benzaldehyde and von Brüning's methylsemicarbazide (*loc. cit.*) in molecular proportion. After the alcohol had been removed by steam distillation, the solution, on cooling, deposited crystals, which, after repeated recrystallisation from alcohol, formed long, white needles melting at 218—219°. The solubility in various solvents, and the behaviour towards alkalis, Fehling's solution, and silver nitrate were the same as described above for phenylmethylhydroxytriazole prepared from benzalmethylsemicarbazone.

0·2128 gave 0·4800 CO_2 and 0·1017 H_2O. C = 61·51 ; H = 5·31.

0·1587 „ 32·8 c.c. moist nitrogen at 11·5° and 745·5 mm. N = 24·15.

$C_9H_9ON_3$ requires C = 61·71 ; H = 5·14 ; N = 24·00 per cent.

The silver derivative was dried at 110°.

0·3315 gave 0·1269 Ag. Ag = 38·28.
$C_9H_8ON_3Ag$ requires Ag = 38·30 per cent.

The acetyl derivative had the same solubilities and crystalline appearance as the compound described on p. 663. It melted at 72—73°, and was hydrolysed by boiling with water.

0·1756 gave 0·3908 CO_2 and 0·0822 H_2O. C = 60·69; H = 5·20.
$C_{11}H_{11}O_2N_3$ requires C = 60·82; H = 5·07 per cent.

That the phenylmethylhydroxytriazole prepared from methylhydrazine is identical with that obtained by synthesis from nitrosomethylurea is shown, not only by the melting points and general behaviour of the two substances and by the characteristic crystalline appearance and melting points of their acetyl derivatives, but also by the following report by Professor Lewis, who kindly examined the crystals for us, and to whom our thanks are due.

Of the crystals submitted to Professor Lewis those of the phenylmethylhydroxytriazole derived from nitrosomethylurea were labelled "$1CH_3$:3Ph," those of the hydroxytriazole from methylhydrazine were labelled "$1CH_3$:5Ph."

"The crystals labelled $1CH_3$:3Ph and $1CH_3$:5Ph are, so far as observations can be made, identical. The crystals of the latter substance are ill developed, and so fragile that on most of them only the prism faces are to be seen. On one of them a small terminal face was found. The crystals are oblique, as is proved by the fact that when the crystal is

β 80°9′; $a:b:c = 0{\cdot}87708:1:0{\cdot}34946$.
$100 \wedge 101 = 59°58{\cdot}25'$, $101 \wedge 001 = 20°10{\cdot}75'$, $010 \wedge 111 = 73°10'$.

	"$1CH_3$:3Ph."				"$1CH_3$:5Ph."	
		Calculated angles.	Observed angles. Means.	Observed angles. Extreme measurements.	First crystal.	Second crystal.
bm	010 : 110	49°10′	49°18′	48°36′—50° 1′		
mm'	110 : $\bar{1}10$	98 20	97 55	97 14 —98 36	101°50	100°24′
mm_1	110 : $1\bar{1}0$	81 40	81 57	81 24 —82 30	78 2	79 34
bn	010 : 011	71 0	71 3			
nn'	011 : $0\bar{1}1$	38 0	37 43			
mn	110 : 011	84 49	84 21			85 31
nm_{11}	011 : $\bar{1}10$	95 11	95 50			94 59
$n'n'$	$\bar{1}10$: $0\bar{1}1$		94 48			
$n'm_1$	$0\bar{1}1$: $1\bar{1}0$	84 49	85 5			

placed between crossed nicols resting on one of the prism faces the direction of extinction is inclined to the edge at an angle of nearly 49°; and two prisms, one of each substance, placed side by side in the polariscope, extinguished the light simultaneously. The habit is one of long, four-faced needles terminated at the free end by two small, triangular planes; occasionally the plane of symmetry is also developed. The following elements were determined by measurement of one of the crystals of '$1CH_3$:3Ph.' The measurements of '$1CH_3$:5Ph' on two crystals are given in the last column of the table."

C-Phenyltriazole, $C_6H_5\cdot C\begin{matrix}=N\\ |\\ NH\cdot N\end{matrix}\!>CH$.

3-Phenyl-1-methylhydroxytriazole was heated with phosphorus pentasulphide at 230—260° for six hours. The resulting dark brown mass was boiled with aqueous potassium carbonate until evolution of gas ceased, and the strongly alkaline liquid repeatedly extracted with ether. The ethereal solution was dried over potassium carbonate and evaporated; the residue, dissolved in benzene and precipitated by addition of light petroleum, formed crystalline nodules which melted at 118·5—119°.

0·1614 gave 0·3930 CO_2 and 0·0692 H_2O. C = 66·40; H = 4·76.
0·1196 ,, 30·8 c.c. moist nitrogen at 15° and 732·8 mm. N = 29·05.
$C_8H_7N_3$ requires C = 66·21; H = 4·83; N = 28·96 per cent.

Addition of platinic chloride to a solution of phenyltriazole in hydrochloric acid gave a precipitate of the *platinichloride*, which, on recrystallisation from dilute acid, formed orange crystals.

0·3906 gave 0·1092 Pt. Pt = 27·96.
$(C_8H_7N_3)_2,H_2PtCl_6$ requires Pt = 27·86 per cent.

On adding a solution of potassium cyanate to phenyltriazole dissolved in dilute hydrochloric acid, a white precipitate was formed, which, on recrystallisation from benzene and light petroleum, gave small, white needles which melted at 146—147°.

Action of Benzaldehyde on von Brüning's Methylsemicarbazide.

Benzaldehyde and methylsemicarbazide, in molecular proportion, were dissolved in alcohol, and evaporated on the water-bath to dryness; the residue, on recrystallisation from benzene and light petroleum, yielded white, delicate needles which melted at 158—159°, and had the appearance of benzal-2-methylsemicarbazide.

0·1490 gave 0·3305 CO_2 and 0·0858 H_2O. C = 60·49; H = 6·39.
$C_9H_{11}ON_3$ requires C = 61·01; H = 6·21 per cent.

Cinnamal-2-methylsemicarbazone,
$C_6H_5 \cdot CH{:}CH \cdot CH{:}N \cdot N(CH_3) \cdot CO \cdot NH_2$.

Nitrosomethylurea was reduced as described above, and the filtrate shaken with cinnamaldehyde. The product separated as a mass of small, yellow needles, and was purified by recrystallisation from water and from dilute alcohol. The yield was about 80 per cent. of the nitrosomethylurea.

0·1550 gave 0·3693 CO_2 and 0·0898 H_2O. C = 64·91 ; H = 6·43.
$C_{11}H_{12}ON_3$ requires C = 65·02 ; H = 6·40 per cent.

Cinnamalmethylsemicarbazone is moderately soluble in boiling water, but almost insoluble in cold water ; it dissolves easily in alcohol. It crystallises in long, white, delicate needles which melt at 155°.

3-Styrenyl-1-methylhydroxytriazole, $C_6H_5 \cdot C_2H_2 \cdot C\begin{matrix} \\ \| \\ \\ \end{matrix}\begin{matrix} N \cdot N(CH_3) \\ \\ N \end{matrix}\!\!>C \cdot OH$.

Cinnamalmethylsemicarbazone was heated with ferric chloride and 70 per cent. alcohol in a closed bottle for one hour at 100°. After addition of water and expulsion of the alcohol by a current of steam, the hot solution was filtered from a small amount of tar. The filtrate, on cooling, deposited the hydroxytriazole, which was dissolved in caustic soda, precipitated by sulphuric acid, and recrystallised from 70 per cent. alcohol. This hydroxytriazole is easily soluble in alcohol and in boiling benzene, but only slightly so in other solvents. It dissolves easily in alkalis. The ammoniacal solution deposits the hydroxytriazole on boiling. The alkaline solutions do not reduce Fehling's solution or silver nitrate.

From 70 per cent. alcohol, the styrenylmethylhydroxytriazole crystallises in beautiful clusters of white needles which melt at 204—205°.

0·1616 gave 0·3896 CO_2 and 0·0772 H_2O. C = 65·74 ; H = 5·31.
0·1628 „ 0·3808 CO_2 „ 0·0782 H_2O. C = 65·47 ; H = 5·34.
0·1416 „ 25·1 c.c. moist nitrogen at 15° and 767 mm. N = 20·97.
$C_{11}H_{11}ON_3$ requires C = 65·67 ; H = 5·47 ; N = 20·89 per cent.

On addition of silver nitrate to a slightly ammoniacal solution of the hydroxytriazole, the silver salt was thrown down as a slightly yellow precipitate ; this was dried at 110° until of constant weight.

0·4533 gave 0·1584 Ag. Ag = 34·94.
$C_{11}H_{10}ON_3Ag$ requires Ag = 35·06 per cent.

The *acetyl* derivative, formed by boiling the hydroxytriazole with acetic anhydride and fused sodium acetate, is easily soluble in alcohol,

ether, benzene, or boiling light petroleum. It forms white crystals which melt at 88—89°, and is easily hydrolysed by boiling with dilute acids.

0·1688 gave 24·7 c.c. moist nitrogen at 8° and 747 mm. N = 17·39
$C_{13}H_{18}O_2N_3$ requires N = 17·28 per cent.

m-*Nitrobenzal-2-methylsemicarbazone*,
$NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot N(CH_3) \cdot CO \cdot NH_2$.

This semicarbazone, formed by reducing nitrosomethylurea and shaking with *m*-nitrobenzaldehyde, was recrystallised from boiling alcohol. It separated rapidly in delicate, canary-yellow needles which melted at 207—208°.

0·1541 gave 0·2758 CO_2 and 0·0627 H_2O. C = 48·81 ; H = 4·52.
0·1546 ,, 33·1 c.c. moist nitrogen at 12° and 756 mm. N = 25·29
$C_9H_{10}O_3N_4$ requires C = 48·64 ; H = 4·50 ; N = 25·22 per cent.

3-m-*Nitrophenyl-1-methylhydroxytriazole*, $NO_2 \cdot C_6H_4 \cdot \overset{\overset{N \cdot N(CH_3)}{\|}}{C} \!\!-\!\!-\!\!- N \!>\! C \cdot OH$.

The nitrobenzalmethylsemicarbazone was oxidised by ferric chloride in alcoholic solution at 100°. After purification in the usual way, the hydroxytriazole was recrystallised from 70 per cent. alcohol. It formed white, delicate needles which melted at 285—285·5°.

0·1777 gave 0·3201 CO_2 and 0·0608 H_2O. C = 49·12 ; H = 3·80.
0·1434 ,, 31·8 c.c. moist nitrogen at 16° and 751 mm. N = 25·52.
$C_9H_8O_3N_4$ requires C = 49·09 ; H = 3·63 ; N = 25·45 per cent.

This hydroxytriazole dissolves in dilute ammonia, forming a yellow solution, and in caustic soda a red solution. These solutions do not reduce Fehling's solution. On addition of silver nitrate to the slightly ammoniacal solution, the silver derivative is thrown down as a light yellow precipitate, which becomes granular on boiling.

0·3700 gave 0·1224 Ag. Ag = 33·08.
$C_9H_7O_3N_4Ag$ requires Ag = 33·03 per cent.

Benzoyl-4-methylthiosemicarbazide, $C_6H_5 \cdot CO \cdot NH \cdot N{:}C(SH) \cdot NH \cdot CH_3$.

4-Methylthiosemicarbazide (Pulvermacher, *Ber.*, 1894, **27**, 622) was dissolved in dry chloroform, and a solution of benzoyl chloride in chloroform added drop by drop. A copious white precipitate was formed, with slight development of heat. On recrystallisation from alcohol, the product formed silky needles which melted at 198°.

0·1772 gave 31·6 c.c. moist nitrogen at 16° and 742·7 mm. N = 20·30
0·2132 ,, 0·2478 $BaSO_4$. S = 15·96.
$C_9H_{11}ON_3S$ requires N = 20·10; S = 15·31 per cent.

2-*Phenyl*-1-*methylmercaptotriazole*, $C_6H_5\cdot\overset{\displaystyle N\!\!-\!\!-\!\!-N}{\underset{\displaystyle \|\quad\ \ }{C\cdot N(CH_3)}}\!\!>\!C\cdot SH$.

Benzoylmethylthiosemicarbazide was heated for some time slightly below its melting point; it fused and lost water. After cooling, the mass was dissolved in hot caustic soda, cooled, filtered, and the product thrown down by addition of hydrochloric acid. After recrystallisation from boiling 70 per cent. alcohol, the mercaptotriazole formed white crystals which melted at 163—164°.

0·1768 gave 34·0 c.c. moist nitrogen at 13° and 738 mm. N = 22·11.
$C_9H_9N_3S$ requires N = 21·99 per cent.

2-*Phenyl*-1-*methyltriazole*, $C_6H_5\cdot\overset{\displaystyle N\!\!-\!\!-\!\!-N}{\underset{\displaystyle \|\quad\ \ }{C\cdot N(CH_3)}}\!\!>\!CH$.

Phenylmethylmercaptotriazole was evaporated down several times with dilute hydrogen peroxide solution on the water-bath. The product, on recrystallisation from ether, formed white, delicate needles which melted at 112—113°.

0·2164 gave 50·2 c.c. moist nitrogen at 15° and 741·7 mm. N = 26·49.
$C_9H_9N_3$ requires N = 26·41 per cent.

Phenylmethyltriazole is easily soluble in alcohol, hot water, or boiling ether, and crystallises out almost completely from the ethereal solution on cooling. It is easily soluble in dilute acids, and is reprecipitated by addition of sodium carbonate.

LXX.—*Preparation of* o-*Dimethoxybenzoin and a New Method of preparing Salicylaldehyde Methyl Ether.*

By James C. Irvine, B.Sc. (1851 Exhibition Research Scholar). (St. Andrews University.)

In the course of recent work, the author had occasion to prepare considerable quantities of the methyl ether of salicylaldehyde, and made a critical examination of the methods hitherto in use.

This substance was first prepared by W. H. Perkin (*Annalen*, 1868, **145**, 302) by acting on the sodium derivative of salicylaldehyde with

methyl iodide dissolved in methyl alcohol. The reaction is conducted in sealed tubes, a temperature of 140° being maintained for some hours. The yield of material is fairly satisfactory but the process is inconvenient when large quantities are required. Voswinckel (*Ber.*, 1882, 15, 2024) modified the method by decomposing the corresponding potassium derivative with methyl iodide in presence of a large excess of methyl alcohol, heating being conducted on the water-bath under the ordinary pressure for many hours. The yields thus obtained vary from 50 to 70 per cent. of the theoretical, but complete decomposition of the potassium salt is only attained after boiling for several days.

In the preparation here described, application was made of the method of alkylating hydroxyl groups by means of dry silver oxide and alkyl iodides (Trans., 1899, 75, 157, 483). By this process, salicylic acid has already been converted into methyl-*o*-methoxybenzoate (Lander, Trans., 1900, 77, 744), but the reaction has not hitherto been applied to hydroxyaldehydes. It was found, however, that very little if any oxidation took place, and a nearly quantitative yield of *o*-methoxybenzaldehyde was obtained.

A preliminary experiment having proved successful, the following proportions were used: Salicylaldehyde, 20 grams (1 mol.); dry silver oxide, 56·8 grams (1½ mols.); methyl iodide, 17·6 grams (3 mols.). The aldehyde and iodide were mixed in a flask provided with an upright condenser, and the thoroughly dried oxide added in small quantities at a time. In a few minutes the liquid commenced to boil vigorously, and the reaction was allowed to complete itself, with the flask immersed in cold water.

After all the oxide had been added, the mixture was warmed for one hour on the water-bath, the product extracted with boiling ether, and filtered from the black silver residues.

The ethereal extract, on testing with ferric chloride solution, was found to contain a trace of unaltered salicylaldehyde, which was removed by shaking with dilute caustic soda; the dried ethereal solution was then distilled. After removal of the ether, the theoretical quantity of alkylated product remained as a brown oil. On distillation, 20 grams of pure substance boiling at 236—238° were obtained representing a 90 per cent yield.

Voswinckel has already recorded the fact that, "when perfectly free from salicylaldehyde," this substance resolves itself very slowly into colourless prisms melting at 37°.

In this case, however, on adding a nucleus the oil immediately solidified to a hard mass of crystals melting at 39—40° which, on analysis, proved to be pure salicylaldehyde methyl ether:

0·208 gave 0·538 CO_2 and 0·113 H_2O. C = 70·54; H = 6·03.
$C_8H_8O_2$ requires C = 70·58; H = 5·89 per cent.

Hydrolysis of the Product.—In order to ascertain if any dimethyl salicylate had been produced in the reaction, 10 grams of the product were boiled for several hours with excess of caustic soda, a little alcohol being added to bring the oil into solution. After nearly neutralising with sulphuric acid, the mixture was evaporated on the water-bath, and the separated oil shaken out with ether. Examination of the extract showed it to contain unaltered salicylaldehyde methyl ether melting at 39—40°.

The alkaline mother liquor was evaporated to a small bulk on the water-bath, and, after acidifying with sulphuric acid, extracted with ether. The ethereal solution, after washing with water and drying over sodium sulphate, gave on evaporation a small quantity of an acid gum, which solidified on cooling to a mass of small prisms. This product, which melted at 92—95°, was recrystallised from absolute alcohol, and afterwards from a mixture of alcohol and light petroleum, when a crop of small, flat prisms was obtained melting at 97—98·5°.

This melting point agrees with that of *o*-methoxybenzoic acid (m. p. 98·5°), a compound produced under these conditions presumably by the hydrolysis of a trace of the methyl ester, but the quantity of the substance obtained did not permit of further examination. It is probable that the production of this impurity was due to the presence of a trace of salicylic acid in the aldehyde used.

The silver oxide reaction is, therefore, capable of being applied as a method of preparing salicylaldehyde methyl ether in a state of purity. Yields of 90 per cent. of the pure substance can be readily obtained, and the process has the additional advantage of being rapid, as all the operations can be completed in one day.

Condensation of Salicylaldehyde Methyl Ether to a Benzoin.

Salicylaldehyde methyl ether has been found to be capable of undergoing the benzoin condensation, yielding a product isomeric with anisoin, which is the corresponding *p*-derivative. The following method of preparation gave the best results.

Salicylaldehyde methyl ether (100 grams), which must be free from salicylaldehyde, was dissolved in the smallest possible amount of 50 per cent. alcohol (300 grams), and the solution vigorously boiled on a sand-bath with potassium cyanide (10 grams). After about two hours' action, the liquid was quickly cooled in a mixture of ice and salt, and the separation of the benzoin promoted by stirring with a glass rod. The solution gradually solidified to a thick mass of golden-

yellow prisms, which was collected on the pump and freed from adhering oil by pressing on a porous plate. The crude product may afterwards be purified by recrystallisation from 50 per cent. alcohol, or better still from ether, in which it is only sparingly soluble.

After the addition of a little more potassium cyanide, the mother liquors were boiled up a second and third time and small additional crops of benzoin thus obtained. The yield of crude product in this case was 64 grams, but the average yield is somewhat lower, amounting to 55 per cent. of the theoretical. When pure, the benzoin was obtained as almost colourless prisms melting at 101·5°; these, however, turned slightly yellow on exposure to light. Analysis of a sample dried in a vacuum gave figures corresponding to those required for *o*-dimethoxybenzoin, $CH_3O \cdot C_6H_4 \cdot CH(OH) \cdot CO \cdot C_6H_4 \cdot OCH_3$.

0·1362 gave 0·3520 CO_2 and 0·0745 H_2O. C = 70·48; H = 6·07.
0·2700 „ 0·6970 CO_2 „ 0·1440 H_2O. C = 70·41; H = 5·92.
$C_{16}H_{16}O_4$ requires C = 70·59; H = 5·88 per cent.

The dark brown, uncrystallisable mother liquors obtained in the above preparation appear to be extremely complex, and examination showed them to contain no unaltered aldehyde ether.

Dimethoxybenzoin has the usual reactions of such substances, and its oxidation and reduction products have already been studied, the latter affording results of considerable interest which I hope to publish shortly.

In order to confirm the *ortho*-nature of the compound, experiments were made with the view of isolating *o*-methoxybenzoic acid as one of the products of oxidation. As ortho-compounds are readily converted into carbon dioxide by oxidising agents, the process had to be conducted carefully, and a large number of experiments were made ere the desired result was obtained. The following process was found to give satisfactory results.

The dimethoxybenzoin was mixed with the calculated amount of potassium permanganate in aqueous solution, some sulphuric acid was added, and the mixture allowed to stand for two hours surrounded by ice-cold water. A considerable quantity of carbon dioxide was evolved and the liquid became colourless. The solution was filtered from the residue, which examination proved to be the impure benzoin. The filtrate was extracted with ether and the *acid* solution thus obtained, after drying over sodium sulphate, evaporated in a current of air. A gummy mass of prisms remained, which, after drying on a porous tile in a vacuum, was recrystallised twice from dilute alcohol. Another recrystallisation from a mixture of alcohol and light petroleum gave a product with the constant melting point 97—98°. This agrees with the melting point (98·5°) of *o*-methoxybenzoic acid. Analysis of a sample dried in a vacuum gave:

C = 62·85 per cent ; H = 5·40 per cent.

$C_8H_8O_3$ requires C = 63·15 per cent ; H = 5·26 per cent.

This result, in which the ortho-nature of the benzoin is substantiated, is important on account of certain abnormalities which the compound showed on reduction.

Preparation of o-Dimethoxybenzoin Methyl Ether.

A reaction of the benzoin which may be conveniently mentioned here is its conversion into a methyl ether. The ethyl and methyl ethers of ordinary benzoin have already been prepared by E. Fischer (*Ber.*, 1893, **26**, 2412) by the hydrochloric acid method, and the alkylating effect of a mixture of dry silver oxide and methyl iodide has also been applied by Lander (*loc. cit.*) in the preparation of benzoin methyl ether. Lander found, however, that partial disruption of the molecule took place with formation of benzaldehyde and methyl benzoate. The dimethoxybenzoin, however, proved to be more stable, and the alkylation by this process gave a quantitative yield of the methyl ether.

Six grams of dimethoxybenzoin were dissolved in excess of methyl iodide by warming on the water-bath. On the gradual addition of 22 grams of dry silver oxide, a feeble reaction set in, which was continued by warming on the water-bath under a condenser for 30 minutes. The product was then extracted with boiling ether, and the filtered solution decolorised by shaking with sodium thiosulphate. After drying, the ethereal solution was evaporated to dryness on the water-bath to expel unaltered methyl iodide. The residual oil on cooling solidified to a mass of beautiful prisms, which after subsequent recrystallisation from ether proved to melt constantly at 59—60°. On analysis of the substance dried in a vacuum :

0·204 gave 0·531 CO_2 and 0·116 H_2O. C = 70·99 ; H = 6·31.

0·1890 ,, 0·4945 CO_2 ,, 0·1100 H_2O. C = 71·35 ; H = 6·46.

$C_{17}H_{18}O_4$ requires C = 71·32 ; H = 6·29 per cent.

The methyl ether crystallises in prisms from its solution in alcohol, ether, or carbon disulphide and distils in a vacuum unchanged. The yield of substance in the above preparation was almost quantitative.

In conclusion, I wish to express my thanks to Prof. Wislicenus, in whose laboratory this investigation was carried out, for the interest he has taken in the progress of the research.

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LXXI.—*Researches on Moorland Waters. Part II. On the Origin of the Combined Chlorine.*

By William Ackroyd, F.I.C.

Given a reservoir of water of a capacity of 640½ million gallons, with a chlorine figure of 1·188 per 100,000 and therefore containing 55 tons of common salt continually being carried away and continually being replenished, with a gathering ground on a saltless area of Millstone Grit and Yoredale Rocks, the question not unnaturally arises, Where does all the salt come from? Such are the conditions at Widdop, on the Yorkshire border, some 7 miles from Burnley, and 12 miles from Halifax at an altitude of 1050 feet above sea level. The problem, which had presented itself to me for some time, acquired an added interest last year from its bearing on chemico-geological speculation (compare Joly "On the Geological Age of the Earth," *B. A. Report*, 1900, pp. 369—379).

To arrive at an answer, chlorine determinations of the reservoir water have been made weekly during the winter months 1900—1901 and compared with the figures yielded by water from a rain-gauge kept near the reservoir. The estimations were made with silver nitrate and potassium chromate without previous concentration, as occasionally less than 10 c.c. of water was available for a test. During the period of testing, one large sample of water was kept for chlorine estimations as a check against the variable data which follow, and at the same time samples were examined from four other gathering grounds to the East; daily tests were also made of the Halifax rainfall collected at Belle Vue Museum. The Widdop figures are given on p. 674.

During the week ending December 24th there was a violent storm from the S.W., presumably bearing salt spray from the Irish Sea, about 40 miles away. Some of the other high figures are, perhaps, to be accounted for by salt-charged, fine dust being brought down by comparatively light rains, that is, a low rainfall. It appears highly probable that the influence of Lancashire towns is a negligible quantity, because the ground investigated, like others far removed from all possibility of town influence, is included in the Yorkshire unit iso-chlor area (Ackroyd, *B. A. Report*, 1900, p. 695). The high chlorine figures also synchronise with similarly high chlorine figures obtained for the other gathering grounds further east in the course of the work.

The conclusions to be drawn are:

1. That the combined chlorine in the reservoir water is wholly derived from rain-water.

Week ending	Chlorine, parts per 100,000.		Rainfall in inches.
	In reservoir water.	In rain-gauge water.	
1900:			
November 12	1·2	0·8	2·05
,, 26	1·0	1·0	0·87
December 3	1·0	0·5	1·29
,, 10	—	0·2	1·28
,, 17	1·1	0·2	0·51
,, 24	1·15	3·3	0·45
,, 31	1·1	1·1	2·20
1901:			
January 7	1·2	1·2	0·02
,, 14	1·3	6·5	0·15
,, 21	1·25	0·85	1·15
,, 28	1·25	1·75	1·55
February 4	(?) 1·4	0·8	0·44
,, 11	1·2	1·75	0·09
,, 18	1·3	—	—
Average	1·188	1·53	

2. That the quantity of chlorine, 1·188 parts per 100,000, in so large a body of reservoir water closely approximates to a yearly average for the rainfall of the gathering grounds, it being so much in excess as is due to concentration arising from evaporation. Deducting 10 per cent. for evaporation and calculating for a rainfall of 43·17 inches, it is equal to an annual deposit of 172·3 lbs. of common salt per acre.

3. That the chlorine in the winter rainfall is in excess of the average for other seasons of the year, as has been found in other parts of the country (Kinch, Trans., 1883, **51**, 94; Lawes, Gilbert, and Warington, *J. Roy. Agric. Soc. Eng.*, 1883, [ii], **19**, 313, quoted by Kinch).

For the trouble involved in the conveyance of weekly samples from the various gathering grounds during the winter weeks, I have to thank Mr. J. A. Paskin, C.E., Waterworks Engineer for the Halifax Corporation, and also the Assistant Engineer, Mr. R. J. Hartley. I have also to acknowledge my indebtedness to Mr. J. Whiteley, of Belle Vue Museum (a Second Class Meteorological Station), who has helped me with rain-samples and meteorological data in the course of this work.

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LXXII.—*On the Estimation of Cocaine and on Cocaine Hydriodide Periodide.*

By W. Garsed, Salters' Company's Research Fellow in the Research Laboratory of the Pharmaceutical Society of Great Britain, and J. N. Collie, F.R.S.

The following communication is the result of some work which was undertaken at the request of the British Medical Council, in order to ascertain whether cocaine could be estimated in small quantities with a fair amount of accuracy. We have not attempted to estimate cocaine when mixed with those other alkaloids, cinnamyl- and isatropyl-cocaine, &c., with which it is associated in coca leaves, but have limited our experiments to pure cocaine, and the alkaloids, benzoylecgonine and ecgonine, which are products of hydrolysis of pure cocaine.

The results of these experiments may be briefly summarised as follows.

When a solution containing about 1 per cent. of cocaine base (dissolved in water as a salt) is titrated by the addition of $N/10$ iodine until the supernatant liquid contains excess of iodine, and, after filtering off the precipitated cocaine hydriodide periodide, the excess of iodine left in solution is estimated by means of $N/10$ sodium thiosulphate, the amount of cocaine present can be calculated on the assumption that all the iodine used has gone to form a compound, $C_{17}H_{21}O_4N,HI,I_2$.

It was found in practice that when the hydrochloride or sulphate was used, double decomposition with the potassium iodide in the $N/10$ iodine solution occurred, and that therefore, for every molecular quantity of iodine used, one molecular quantity of cocaine was necessary.

This cocaine hydriodide periodide is a remarkably stable, crystalline compound, and can be obtained in large, glistening crystals of constant composition. It was found that the presence of ecgonine, even in considerable quantities, did not interfere with the estimation, for any compound that may be produced remains in solution.

Benzoylecgonine, however, does interfere to a considerable extent, but by making use of the fact that this base is practically insoluble in ether, a separation from the cocaine can be effected by this means, and subsequent titration with iodine will give the quantity of cocaine present.

Experimental.

The cocaine used was in the form of the pure hydrochloride obtained from Hopkins and Williams, and after most careful testing

was considered to be pure; it answered to Maclagan's and the potassium permanganate tests. This hydrochloride, when dissolved in water, was found to be precipitated by a solution of iodine in potassium iodide even when the cocaine solution was diluted to 1 in 50,000 of water. This, therefore, is a very delicate test, and we determined to try whether a quantitative method for the estimation of cocaine could be based on it.

First Series of Experiments.—To ascertain how much iodine was absorbed by a neutral solution of cocaine hydrochloride when added to $N/10$ iodine solution.

The strength of the cocaine salt solution was always the same, 1 gram of cocaine base in 100 c.c. of aqueous solution. The iodine solution was decinormal, and in every case the cocaine salt solution was run into excess of iodine solution. The precipitate was filtered off through purified asbestos, and the excess of iodine determined by titration with $N/10$ thiosulphate solution. In every case, 10 c.c. of the cocaine solution were used.

Expt.	C.c. of iodine solution.	C.c. used.	Iodine used (gram).	Atomic ratio of cocaine to iodine.
1	15	10·88	0·143	1 : 3·4
2	20	13·5	0·177	1 : 4·2
3	25	14·53	0·191	1 : 4·5
4	30	14·87	0·195	1 : 4·6
5	35	14·97	0·1965	1 : 4·7
6	35	14·73	0·1932	1 : 4·6
7	40	15·3	0·201	1 : 4·8
8	45	15·56	0·204	1 : 4·9
9	50	15·57	0·2046	1 : 4·9
10	60	15·9	0·209	1 : 5·0

From 3 to 5 hours elapsed between precipitation and filtration in every experiment except Nos. 3 and 10. In the case of No. 3, 24 hours, and in that of No. 10, 17 hours elapsed before the precipitate was filtered off. From these results, it will be seen that no definite amount of iodine is taken up by the cocaine, and that the larger the excess of iodine solution used, the larger the amount of iodine absorbed by the hydriodide of the base.

The precipitated iodine compound was a black, tarry, semi-fluid mass. On treatment with ether, a large quantity of iodine was extracted, leaving a crystalline residue, which, on recrystallisation from alcohol, was obtained at once and without difficulty in the form of glistening, purple crystals melting at 161°. It can easily be prepared in quantity by adding a solution of iodine in potassium iodide to a solution of cocaine hydrochloride. From 4·5 grams of the hydro-

chloride, taking no special precautions, 6 grams of the pure crystalline substance were obtained.

It was found that this compound was always produced, no matter what salt of cocaine was operated upon, for if the sulphate or the chloride were used, the potassium iodide in the iodine solution gave potassium sulphate or chloride, and cocaine hydriodide by double decomposition, and the precipitated iodine compound was entirely free from either sulphuric or hydrochloric acids.

On analysis, the following numbers were obtained :

(1) Prepared from the hydrochloride. I = 54·2.
(2) ,, ,, sulphate. I = 55·2.
(3) ,, ,, ,, and recrystallised. I = 55·6.
(4) ,, ,, ,, C = 29·6 ; H = 3·3 ; N = 2·1.

$C_{17}H_{21}O_4N,HI_2$ requires C = 29·8 ; H = 3·1 ; N = 2·0 ; I = 55·6 per cent.

The iodine in the crude, uncrystallised precipitate, obtained by adding iodine to a solution of the sulphate, was estimated. I = 55·6.

That the hydriodide of cocaine is produced by the addition of potassium iodide to a solution of the hydrochloride of cocaine, is easily proved, for if strong solutions of the two salts are mixed, the sparingly soluble cocaine hydriodide crystallises out.

Second Series.—In order to see whether the use of more dilute solutions would affect the results, the following experiments were made. A solution containing 1 gram of cocaine base as hydrochloride in 1000 c.c. water was added to *N*/100 iodine solution. In each case, 10 c.c. of the cocaine solution were used.

Expt.	C.c. of iodine solution.	C.c. used.	Iodine used (gram).	Atomic ratio of cocaine to iodine.
1	20	7·39	0·00961	1 : 2·3
2	30	9·25	0·0120	1 : 2·8
3	40	10·22	0·01329	1 : 3·2
4	50	9·29	0·01210	1 : 2·9
5	30	13·80	0·01795	1 : 4·3
6	40	13·33	0·01734	1 : 4·1
7	50	14·90	0·01938	1 : 4·6

In the first four experiments, the precipitate and iodine solution were allowed to stand for 12 hours before filtering, in No. 5 for 5 hours, and in Nos. 6 and 7 for 48 hours.

Third Series.—In this series, a stronger solution of cocaine hydrochloride was used, containing 1 gram of base in 100 c.c. of solution. This was added to a weak solution of *N*/100 iodine.

One c.c. of cocaine solution was used in each experiment.

Expt.	C.c. of iodine solution.	C.c. used.	Iodine used (gram).	Ratio of cocaine to iodine.
1	30	13·50	0·01756	1 : 4·2
2	40	13·30	0·01730	1 : 4·1
3	50	13·30	0·01730	1 : 4·1

Fourth Series.—In this series, a solution of cocaine hydriodide containing 1 gram of base in 100 c.c. was added to $N/10$ iodine, but as a result of seven experiments, the ratio of cocaine to iodine absorbed varied from 1 : 3·8 to 1 : 4·6.

In all these experiments, the cocaine hydrochloride solution had been run into the iodine solution; the reverse was now tried. The cocaine hydrochloride solution contained 1 gram of base in 100 c.c., and to this was added $N/10$ iodine. The precipitate was now found to be quite different, as, instead of a black, tarry substance, a pale brown, flocculent precipitate was obtained. Moreover, the precipitated iodine compound was, in each case, collected, dried, and weighed; to obtain precipitates of definite composition, the iodine solution must be run in drop by drop with constant agitation. In every experiment, 10 c.c. of cocaine solution were used.

Expt.	C.c. of iodine solution used.	Atomic ratio of cocaine to iodine.	Weight of ppt. (gram).	Calculated amt. (gram).
1	6·47	1 : 1·96	0·2170	0·2252
2	6·5	1 : 1·97	0·2156	0·2252
3	6·6	1 : 2·0	0·2176	0·2252
4	6·47	1 : 1·96	0·2198	0·2252
5	6·62	1 : 2·0	0·2226	0·2252
6	6·63	1 : 2·0	0·2226	0·2252

In order to further test this method, solutions were made up, of which the operator did not know the strength. The results were as follows:

Found 3·25, 3·35, 3·25 grams, mean 3·28 grams, of cocaine hydrochloride in 500 c.c. of the solution. The real strength was 3·25 grams of cocaine hydrochloride in this volume.

In some more determinations of the same kind, 1·094 and 1·091 grams, mean 1·0925 grams, of cocaine hydrochloride were found in a solution into which 1·100 grams had been put. Several more experiments were made with the same result, which showed that by this process a method possessing a fair degree of accuracy had been devised.

The next series of determinations were made with mixtures of cocaine, benzoylecgonine, and ecgonine. The benzoyl ecgonine was prepared by heating pure cocaine on the water-bath with water until it had all dissolved. On concentration, benzoylecgonine crystallised

out from the solution. From 6 grams of cocaine hydrochloride, 3·35 grams of benzoylecgonine melting at 197—198° were obtained, the theoretical amount being 5·05 grams.

Although this base forms a periodide, yet the salt is much more soluble in water containing potassium iodide than the corresponding cocaine compound. For instance, a $N/10$ solution of iodine added to a solution of a salt of benzoylecgonine (1 in 500) gave an opalescence, and finally a precipitate. This disappeared on addition of more potassium iodide to the solution or on dilution with more water.

Ecgonine was prepared by boiling 5 grams of cocaine hydrochloride with fuming hydrochloric acid. The resulting benzoic acid was removed (it weighed 1·7 grams, theoretical amount 1·8), and the solution evaporated. The ecgonine hydrochloride was recrystallised from alcohol, and gave all the tests for the pure salt.

Before experimenting with mixtures of cocaine with ecgonine and benzoylecgonine, the action of iodine was tried on solution of ecgonine salts. To 5 c.c. of ecgonine hydrochloride solution, containing 0·01 gram of base, 25 c.c. of $N/100$ iodine were added carefully, but not even an opalescence was produced. On titrating back with $N/10$ thiosulphate solution, 24·85 c.c. were required. In a second experiment, 5 c.c. of the same solution treated with 21 c.c. of $N/100$ iodine solution required 20·99 c.c.

Even when stronger solutions of ecgonine are used, containing 1 gram in 100 c.c., the addition of iodine produces merely an opalescence, which disappears on adding a little potassium iodide.

Several estimations of cocaine were made in mixtures containing various quantities of cocaine and ecgonine hydrochlorides.

	Present.		Found.	
	Ecgonine base.	Cocaine base.	Cocaine base.	Error per cent.
1.	0·02 gram	0·02 gram	0·01975 gram	−1·2
2.	0·06 „	0·02 „	0·02024 „	+1·2
3.	0·01 „	0·03 „	0·02923 „	−2·5

From these results, it seems that cocaine can be estimated in presence of ecgonine by this iodine method. It has been already stated that, if sufficient potassium iodide is present in the iodine solution, benzoylecgonine is not precipitated; even a solution containing 1 in 100 of the base with excess of potassium iodide is not precipitated by iodine. The iodine solution itself contained potassium iodide, the amount being about 2·5 per cent.

Estimation of Cocaine in a Solution containing the Hydrochlorides of Cocaine, Benzoylecgonine, and Ecgonine.

(1) Fifteen c.c. of a solution containing 0·01 gram of each base were taken. To this was added 0·25 gram of potassium iodide. After titration with $N/100$ iodine, 0·0127 gram of base was found.

(2) Another 15 c.c. were used, 0·5 gram of potassium iodide was added, and after titration 0·0118 gram of base was found.

(3) Another 15 c.c., to which was added 1 gram of potassium iodide, gave 0·0118 gram of base.

Evidently, the cocaine periodide carries down some of the benzoylecgonine periodide with it.

Some further experiments were undertaken to find out exactly how much potassium iodide would prevent the precipitation of benzoylecgonine by means of $N/100$ iodine. Four experiments were made, using in each case 5 c.c. of a solution of benzoylecgonine hydrochloride containing 0·01 gram of base.

(1) 0·25 gram of potassium iodide used; after the addition of a few drops of iodine solution, a permanent precipitate was obtained.

(2) 0·5 gram of potassium iodide used; on adding iodine solution, similar result.

(3) 1 gram of potassium iodide used; no precipitate until 5 c.c. of iodine were added.

(4) 1·5 gram of potassium iodide used; no precipitate even after the addition of 20 c.c. of iodine solution.

One more determination was therefore made with the mixture mentioned above containing 0·01 gram of each of the three bases as hydrochlorides. After titration, 0·0114 gram was found. This result was still too high. But a blank experiment, made under exactly the same conditions with a solution containing 0·01 gram of cocaine alone, gave 0·0092 gram. The estimation of cocaine in presence of benzoylecgonine by this iodine method seems to be impossible, although cocaine in presence of ecgonine can be easily determined.

However, there is a way out of the difficulty, for both ecgonine and benzoylecgonine are not extracted from an alkaline solution by either ether or light petroleum.

0·1 gram of benzoylecgonine was dissolved in about 5 c.c. of water acidified with sulphuric acid; the solution was then made alkaline and twice shaken out with ether. The residue after evaporation of the ether weighed 0·0002 gram.

The same experiment repeated with light petroleum yielded no residue. Exactly the same results were obtained with ecgonine,

the ether residue being 0·0002 gram, and that from light petroleum *nil*.

A mixture of 0·1 gram of cocaine, 0·1 gram of benzoylecgonine, and 0·1 gram of ecgonine similarly treated, on being shaken out twice with ether, yielded a residue weighing 0·1008 gram. This residue was dissolved in water and hydrochloric acid and titrated with iodine solution. It gave 0·0965 gram of cocaine.

RESEARCH LABORATORY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

LXXIII.—*Note on Acetonylacetone.*

By THOMAS GRAY.

THE physical constants of acetonylacetone, determined with a product which had been carefully purified by repeated fractionation under diminished pressure, appear in a paper by Knorr (*Ber.*, 1900, 33, 1219).

As the ketone which was used for this purpose gradually acquired a yellow tinge, it was considered desirable to attempt further purification by conversion into the sodium bisulphite compound, and to redetermine the constants of the ketone isolated therefrom.

The bisulphite compound was prepared in the usual way, pressed in a hydraulic press, and dried in a vacuum over sulphuric acid. On analysis:

0·5368 gave 0·2222 Na_2SO_4. $Na_2O = 18·07$.

$C_6H_{10}O_2,2NaHSO_3,H_2O$ requires $Na_2O = 18·23$ per cent.

The ketone was regenerated from the bisulphite compound by boiling with potassium carbonate solution, and extracted with ether from free alcohol.

The index of refraction, $n_D^{20°}$, of the product was 1·423. It was redistilled under 300 mm. pressure, and collected in two fractions:

Fraction I.	$n_D^{20°} = 1·4230$
Fraction II.	$n_D^{20°} = 1·4232$

The value of the specific gravity was the same as that previously obtained.

Table of constants.

Specific gravity, $d_4^{20°}$	0·973
Index of refraction, $n_D^{20°}$	1·4232
Molecular refraction, $\mathfrak{M}_{Na}$	29·85
The ketonic formula, $CH_3·CO·CH_2·CH_2·CO·CH_3$, requires	30·10
,, enolic ,, $CH_3·C(OH):CH·CH:C(OH)·CH_3$,,	31·98

The behaviour of acetonylacetone towards alkali and metallic sodium is noteworthy, as it affords an explanation of the failure of a number of condensations which were attempted according to Claisen's method. Interaction with ethyl formate, benzoate, acetate, and succinate resulted in the formation of resinous substances. In the case of ethyl oxalate already reported (*Ber.*, 1900, **33**, 1220), the reaction, however, proceeded normally.

If a few drops of caustic soda solution are added to acetonylacetone, the ketone rapidly acquires a yellow colour, and a brown resin separates out on standing.

Metallic sodium also reacts readily with the ketone in ethereal solution, and is gradually converted into a brown powder, from which, on solution in water and acidification, a resinous mass is obtained.

Hydrogen chloride and concentrated sulphuric acid rapidly resinify acetonylacetone. In both cases, a dark-coloured semi-solid mass was formed. This yielded, on addition of water, a black, charcoal-like mass from which a yellow substance was extracted by alcohol. As this could not be obtained in a crystalline condition, it was not further examined.

The results of numerous experiments with acetonylacetone lead me to conclude that the ketone will not prove of general value for synthetical purposes. The work of Knorr has made it possible to prepare large quantities of the substance conveniently, and thus opened up an apparently promising field for research. On this account, it seems desirable that the great instability of acetonylacetone towards alkalis and acids should be placed on record.

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LXXIV.—*Condensation of Acetonylacetone with Hydrazine Hydrate.*

By THOMAS GRAY.

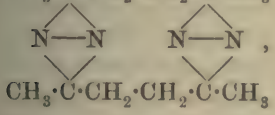
ACETONYLACETONE reacts readily with hydrazine hydrate with development of heat. If the two substances are mixed in molecular proportion, a basic compound possessing the formula $C_{12}H_{20}N_4$ is formed. Interaction with excess of acetonylacetone results in the formation of a highly unstable, crystalline substance, the composition of which is expressed by the formula $C_{12}H_{24}N_6$.

The condensation in molecular proportion may theoretically take

place in a variety of ways. The observation by Knorr, that phenylaminodimethylpyrrole is produced by the action of phenylhydrazine on acetonylacetone, points to the probable formation of aminodimethylpyrrole, $\begin{matrix}CH{:}C(CH_3)\\ CH{:}C(CH_3)\end{matrix}\!\!>\!N{\cdot}NH_2$, whilst the formation of triphenyldihydropyridazine from dibenzoylphenylethane (Smith, *Annalen*, 1896, 289, 316), $\begin{matrix}C_6H_5{\cdot}CH{\cdot}CO{\cdot}C_6H_5\\ CH_2{\cdot}CO{\cdot}C_6H_5\end{matrix} \rightarrow \begin{matrix}C_6H_5{\cdot}C{=}C(C_6H_5){\cdot}NH\\ CH{:}C(C_6H_5){\cdot}NH\end{matrix}$, makes it possible that dimethyldihydropyridazine, $\begin{matrix}CH{:}C(CH_3){\cdot}NH\\ CH{:}C(CH_3){\cdot}NH\end{matrix}$, may be a product of the condensation.

A number of determinations of the freezing point of solutions of the substance in benzene and in water, and of the boiling point of the ethereal solution, gave values for the molecular weight which were twice as large as that required by the formulæ given above.

The structure of the condensation product is, therefore, probably expressed by one of the two following formulæ:



$$\begin{matrix}NH{\cdot}C(CH_3){:}CH{\cdot}CH{:}C(CH_3){\cdot}NH\\ NH{\cdot}C(CH_3){:}CH{\cdot}CH{:}C(CH_3){\cdot}NH\end{matrix}.$$

Experimental.

Condensation of Acetonylacetone and Hydrazine Hydrate in Molecular Proportion.

Fifteen grams of hydrazine hydrate were slowly added to 34·2 grams of acetonylacetone cooled in water, and the mixture was then allowed to stand for about an hour. It was afterwards dissolved in ether, dried over potassium carbonate, and distilled under diminished pressure in hydrogen. The bulk of the product (24·5 grams) distilled over between 160° and 175° under 20 mm. pressure. This was rectified by distillation, and a pure product boiling at 157—158° under 13 mm. pressure was obtained. The distillate crystallised in the condensing tube at the beginning of the distillation, but after it had been melted it remained liquid for several days.

The substance thus prepared was a slightly yellow, highly viscous oil, which, after having stood for several days at the ordinary temperature, began to crystallise, and was slowly converted into a solid, white, crystalline mass composed of rhombohedral crystals. On analysis:

0·2168 gave 0·5192 CO_2 and 0·1702 H_2O. C = 65·31; H = 8·72.
0·2156 „ 0·5160 CO_2 „ 0·1796 H_2O. C = 65·27; H = 9·25.
0·1784 „ 38·6 c.c. nitrogen at 15° and 757 mm. N = 25·24.
$C_{12}H_{20}N_4$ requires C = 65·45; H = 9·09; N = 25·45 per cent.

Determination of molecular weight:

Wt. of subst.	Wt. of solvent.	Depression of freezing point.	*m*.
0·3468	12·98 benzene	0·64°	208
0·2344	14·67 water	0·13	227
0·5164	14·67 „	0·29	224

The values 222, 227, and 200 were obtained by Walker and Lumsden's modification of Landsberger's method, using ether as the solvent. $C_{12}H_{20}N_4$ requires $m = 220$.

The condensation product is readily soluble in water, alcohol, ether, or benzene. It rapidly absorbs oxygen from the air, becoming dark brown in colour, and behaves as a reducing agent. On adding silver nitrate or Fehling's solution to an aqueous solution of the substance, no immediate change is noticed, but reduction takes place slowly in the cold and quickly on boiling. The aqueous solution is neutral to litmus, but the substance possesses basic properties. On addition of an ethereal solution of the base to excess of a solution of hydrogen chloride in ether, a white, crystalline precipitate of the hydrochloride is produced.

The *hydrochloride* prepared in this way was washed with dry ether and dried in a vacuum, first over concentrated sulphuric acid, and finally over soda lime to remove any excess of acid; it is highly deliquescent. On analysis:

0·5166 gave 0·5073 AgCl. HCl = 24·97.
0·4258 „ 0·4185 AgCl. HCl = 24·99.
$C_{12}H_{20}N_4,2HCl$ requires HCl = 24·91 per cent.

The *platinichloride* was obtained as a sparingly soluble, yellow precipitate on addition of platinic chloride to an aqueous solution of the hydrochloride. It was washed with water, alcohol, and ether, and dried in a vacuum over sulphuric acid, as it was found to undergo decomposition when heated in an air-bath at 110—120°. On ignition:

0·6148 gave 0·1930 Pt. Pt = 31·39.
$C_{12}H_{20}N_4,H_2PtCl_6$ requires Pt = 31·02 per cent.

Condensation of Acetonylacetone with Excess of Hydrazine Hydrate.

Acetonylacetone (6·3 grams) was gradually added to hydrazine hydrate (6 grams) cooled in water; separation of crystals took place almost immediately, and the mixture quickly solidified, forming a

white, crystalline mass. The crystals were dried on a porous plate and crystallised from methyl alcohol. The substance thus obtained had not a sharp melting point, on account of slight decomposition during the operation of crystallising. It was therefore repeatedly crystallised, and analysed after each crystallisation. On analysis, after one, two, and four crystallisations:

I. 0·163 gave 48·3 c.c. nitrogen at 23° and 748 mm. N = 33·15.
II. 0·184 „ 0·384 c.c. CO_2 and 0·1562 H_2O. C = 56·91; H = 9·43.
0·142 „ 42·2 c.c. nitrogen at 22° and 743 mm. N = 33·19.
III. 0·183 „ 0·3836 CO_2 and 0·1564 H_2O. C = 57·16; H = 9·49.
0·1382 „ 40·4 c.c. nitrogen at 22° and 755 mm. N = 33·18.
$C_{12}H_{24}N_6$ requires C = 57·14; H = 9·52; N = 33·33 per cent.

The substance crystallises from methyl alcohol in prisms melting at 130—132°. It dissolves readily in alcohol, but is only sparingly soluble in water, benzene, or ether. On exposure to air, it acquires a yellow colour and gradually decomposes with liquefaction. It is a powerful reducing agent; platinic chloride is reduced to platinous chloride with evolution of nitrogen, whilst gold chloride, silver nitrate, and Fehling's solution are reduced in the cold. If mercuric oxide is added to a solution of the substance in methyl alcohol, rapid oxidation takes place with evolution of nitrogen. The substance is readily decomposed by acids, with formation of hydrazine salts. Even such feebly acid substances as picric and picrolonic acids effect this decomposition. The picrate had the crystalline form of hydrazine picrate and decomposed at 189—190°.

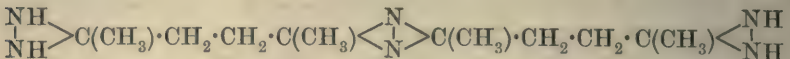
A picrolonate was obtained as a yellow, crystalline precipitate by adding a solution of picrolonic acid in alcohol to an alcoholic solution of the substance. It was found to be identical with hydrazine picrolonate, which was prepared for the purpose of comparison. On analysis:

0·1580 gave 0·2334 CO_2 and 0·0548 H_2O. C = 40·29; H = 3·85.
0·1376 „ 34·6 c.c. nitrogen at 22° and 750 mm. N = 28·35.
$N_2H_4 \cdot C_{10}H_8O_5N_4$ requires C = 40·54; H = 4·05; N = 28·38 per cent.

Hydrazine picrolonate crystallises from alcohol or water in the form of bow-shaped prisms or needles which decompose at 262°. It is sparingly soluble in alcohol and in water.

An attempt to determine the molecular weight of the product of the condensation of acetonylacetone with excess of hydrazine hydrate by the boiling point method, using methyl alcohol as a solvent, was unsuccessful, as the substance was found to undergo decomposition. The sparing solubility of the product in the solvents commonly used for the determination of the freezing point precluded the use of this

method. The analyses show that the reaction took place between 2 mols. of the ketone and 3 mols. of hydrazine hydrate. The structure of the product is, therefore, probably represented by the formula:



The author desires to express his indebtedness to Prof. L. Knorr, at whose suggestion the investigation of the properties of acetonylacetone was undertaken, for his kind advice during the prosecution of the work.

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LXXV.—*Preparation and Properties of* 2 : 6-*Dibromo*-4-*nitrosophenol.*

By MARTIN ONSLOW FORSTER and WILLIAM ROBERTSON, A.R.C.S.

THE observation that camphoroxime is converted into 1 : 1-bromonitrocamphane by the action of an alkaline solution of potassium hypobromite (Trans., 1899, 75, 1141) has led us to examine the behaviour of this agent towards a large number of *iso*nitroso-compounds. Among the first of these was *p*-nitrosophenol, because this substance may be regarded as the simplest of benzenoid oximes in which the nitrogen atom is attached directly to the aromatic nucleus.

When *p*-nitrosophenol is dissolved in caustic potash, and treated with an alkaline solution of potassium hypobromite, lustrous, dark-green leaflets are deposited, consisting of the potassium derivative of dibromonitrosophenol, $C_6H_2Br_2(OH)\cdot NO$, but on examining the literature relating to this substance, we found it so contradictory as to render doubtful the identity of our product.

According to O. Fischer and Hepp (*Ber.*, 1888, 21, 674), a solution of bromine in alcohol converts *p*-nitrosophenol into 2 : 6-dibromo-4-nitrosophenol. These authors mention that it crystallises from dilute alcohol in leaflets, but do not state the temperature at which it melts. Bridge affirms that the method of Fischer and Hepp gives rise to at least two, and perhaps three, compounds (*Annalen*, 1893, 277, 102), and represents the preponderating constituent of the mixture as crystallising from toluene in brown needles, which melt and decompose at 170°. A reference to dibromonitrosophenol is made by Kehrmann

(*Ber.*, 1888, 21, 3318), who treated *m*-dibromoquinone with hydroxylamine hydrochloride, obtaining 2 : 6-dibromo-4-nitrosophenol which, according to this author, crystallises from dilute alcohol in thin, lustrous, pale yellow leaflets, decomposing at 145°, and is "zweifellos identisch" with the compound described by Fischer and Hepp.

The statements of Bridge and of Kehrmann cannot be reconciled with one another, and as they afforded us no assistance, we consider it desirable to place on record an account of the properties of the dibromonitrosophenol in question.

The results of our investigation show that the compound obtained by the action of potassium hypobromite on *p*-nitrosophenol is the potassium derivative of 2 : 6-dibromo-4-nitrosophenol, and that this process for obtaining the substance is a much more satisfactory one than those already described.

Action of Potassium Hypobromite on p-*Nitrosophenol.*

The *p*-nitrosophenol employed in these experiments was prepared from phenol and nitrous acid, according to the directions of von Baeyer and Caro, 150 grams of the nitroso-derivative being obtained from 120 grams of phenol.

Twelve hundred grams of caustic potash were dissolved in 1600 c.c. of water, and allowed to cool; a considerable quantity of crushed ice was added, followed by 800 grams of bromine. The liquid was then poured into a solution of 200 grams of *p*-nitrosophenol in 1000 c.c. of water containing 250 grams of caustic potash. After an interval of 12 hours, a considerable quantity of the green potassium derivative had become deposited, and the deep brown liquid was therefore decanted from the crystals, which were then collected with the aid of a filter pump, and drained on porous earthenware. The dried product weighed 226 grams, but the comparatively low yield, which amounts to only 43 per cent. of that required by theory, is, to some extent, counterbalanced by the pure condition in which the substance is obtained.

When acetic acid is added to an aqueous solution of the potassium derivative, a yellow precipitate of 2 : 6-dibromo-4-nitrosophenol is obtained. This compound crystallises from alcohol and from glacial acetic acid in long, dark brown, prismatic needles, having a violet reflex; it darkens at about 160° and detonates at any temperature between 168° and 175°, according to the rate at which the temperature is raised. On analysis:

0·2164 gave 0·2036 CO_2 and 0·0277 H_2O. C = 25·66; H = 1·42.

0·2239 „ 0·2985 AgBr. Br = 56·73.

$C_6H_3O_2NBr_2$ requires C = 25·62; H = 1·07; Br = 56·94 per cent.

Dibromonitrosophenol is sparingly soluble in hot water, from which

it crystallises in slender, pale yellow needles. It dissolves in sodium carbonate and in concentrated sulphuric acid, from which it is precipitated on adding water.

The *potassium* derivative, produced in the manner described above, forms lustrous green leaflets having a slight bronze reflex. It dissolves very readily in water, forming a deep brown solution which becomes yellowish-green when diluted.

0·2157 gave 0·0549 K_2SO_4. K = 11·41.

$C_6H_2O_2NBr_2K,H_2O$ requires K = 11·57 per cent.

The salt crystallises from water in green leaflets which are so dark as to appear almost black; alkalis precipitate it from aqueous solutions in pale green scales.

The *acetyl* derivative, prepared by heating 5 grams of the dibromonitrosophenol with 50 c.c. of glacial acetic acid and 5 c.c. of acetic anhydride in a reflux apparatus during one hour, is readily soluble in hot alcohol, from which it crystallises in lustrous, crimson needles. It melts and decomposes at 122°.

0·2360 gave 0·2746 AgBr. Br = 49·53.

$C_8H_5O_3NBr_2$ requires Br = 49·53 per cent.

The *benzoyl* derivative, obtained from the potassium derivative by the Schotten-Baumann method, dissolves very sparingly in alcohol; it is moderately soluble in ethyl acetate, from which it crystallises in lustrous, yellow needles melting at 197°.

0·2156 gave 0·2096 AgBr. Br = 41·36.

$C_{13}H_7O_3NBr_2$ requires Br = 41·56 per cent.

Bridge (*loc. cit.*) prepared the benzoyl derivative of dibromonitrosophenol obtained according to the directions of Fischer and Hepp; he states that the substance melts at 191°.

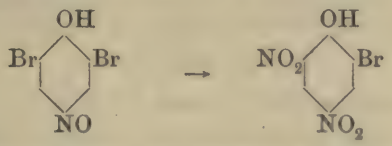
Oxidation of 2 : 6-*Dibromo*-4-*nitrosophenol.*

With the object of ascertaining the position of the substituents in the dibromonitrosophenol obtained by our process, we have oxidised the substance under various conditions, expecting to convert it into 2 : 6-dibromo-4-nitrophenol, which melts at 142°.

The two agents recommended for the oxidation of nitrosophenol to nitrophenol are alkaline potassium ferricyanide, and concentrated nitric acid. Neither of these is suitable to the present case. An alkaline solution of potassium ferricyanide is without action on dibromonitrosophenol unless heated with it, when a very dark, crystalline substance is produced, which is certainly not a dibromonitrophenol. Experiments with potassium permanganate were equally

unsuccessful; oxidation takes place to a considerable extent, but not in the direction required, because the filtrate from the manganese oxide, when acidified with acetic acid, yields unaltered dibromonitrosophenol.

Concentrated nitric acid is, for another reason, equally unadapted to the purpose in view. On treating dibromonitrosophenol with nitric acid (sp. gr. 1·42), a change began at once; at first the liquid was cooled to moderate the action, and finally warmed until the solid dissolved. The crystals which separated from the cold liquid were drained on porous earthenware and recrystallised from alcohol, which deposited aggregates of transparent, canary-yellow prisms melting at 117°. This substance, however, is not a dibromonitrophenol, but a bromodinitrophenol, nitric acid having simultaneously displaced a bromine atom and oxidised the nitroso-group. In view of the fact that 2:4-dibromo-6-nitrophenol melts at the same temperature, we prepared this substance from *o*-nitrophenol and bromine water, and also obtained a specimen of 2-bromo-4:6-dinitrophenol from tribromophenol and fuming nitric acid; on comparing these two substances in turn with the derivative obtained from dibromonitrosophenol and concentrated nitric acid, and observing the melting point of mixtures, it was quite clear that the compound obtained from 2:6-dibromo-4-nitrosophenol in the manner described is 2-bromo-4:6-dinitrophenol.



The oxidation to dibromonitrophenol was ultimately effected by means of dilute nitric acid. Two grams of finely powdered dibromonitrosophenol were suspended in 10 c.c. of nitric acid prepared by diluting 5 c.c. of the concentrated acid (sp. gr. 1·42) with 10 c.c. of water. After an interval of 24 hours, it was noticeable that the greenish colour of the substance had changed to yellow, and when the liquid had remained at the temperature of the laboratory during a period of 66 hours, it was diluted with water; the product, after being twice recrystallised from alcohol, melted at 142°, and decomposed immediately afterwards. It agreed in every respect with a specimen of 2:6-dibromo-4-nitrophenol prepared from tribromophenol and nitric acid according to Armstrong and Harrow's directions (this Journ., 1876, **29**, 477).

Reduction of 2 : 6-Dibromo-4-nitrosophenol.

Fischer and Hepp state that when dibromonitrosophenol is reduced with tin and hydrochloric acid, 2 : 6-dibromo-4-aminophenol is formed, and describe the base as crystallising in faint red prisms which melt at 189°. Following the lines indicated by these authors, we reduced 2 : 6-dibromo-4-nitrosophenol, and obtained a specimen of 2 : 6-dibromo-4-aminophenol crystallising in colourless prisms; the substance has an indefinite melting point, as it darkens gradually when heated, decomposing at about 190°. Crystals deposited from the mother liquor were pale red, but the purified substance is colourless.

The *benzoyl* derivative was prepared by agitating the base with benzoyl chloride in presence of caustic soda, and afterwards saturating the liquid with carbon dioxide. It crystallises from alcohol in slender, white needles melting at 208°; the substance becomes pink on exposure to sunlight.

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LXXVI.—*Alkylation of Acylarylamines.*

By G. DRUCE LANDER.

THE author has shown (Trans., 1900, 77, 737) that by the action of dry silver oxide and ethyl iodide on acetanilide, ethyl *iso*acetanilide, $CH_3 \cdot C_6(OEt):N \cdot CH_5$, can readily be prepared. The alkylation of other acylarylamines by the same means is described in the present paper, imino-ethers having been prepared from acetanilide, aceto-*o*- and -*p*-toluidides, aceto-*α*- and -*β*-naphthalides, benzanilide, ethyl oxanilate, and oxanilide. Several imino-ethers, in which the iminic hydrogen atom is replaced by an aromatic radicle, have been obtained previously, for example, N-phenylformimino-ethers from silver formanilide (Comstock and Klerberg, *Amer. Chem. J.*, 1879, 12, 498); N-phenylbenzimino-ethyl ether from benzimino-ethyl ether hydrochloride and aniline (Lossen, *Annalen*, 1891, 265, 138), and semi-N-phenylamino-oxalic dimethyl ether from methyl dichloro-oxalate and aniline (Anschütz and Stiepel, *Ber.*, 1895, 28, 61; *Annalen*, 1899, 306, 11). The use of an alkyl iodide and dry silver oxide seems, however, to afford a general method for the preparation of imino-ethers of this constitution. Names recalling the iminic character of the ethers described in this paper are used instead of the term alkyl *iso*ether formerly employed.

The most valuable evidence of the constitution of these imino-ethers is afforded by their usually ready hydrolysis by dilute hydrochloric acid into primary arylamine and, according to the conditions observed, either acid and alcohol or ester. All the imino-ethers described in this paper are liquids at the ordinary temperature, as also, apparently, are the N-ethyl acetotoluidides, but the boiling points of the isomeric compounds are widely different. Claisen, in a paper on formanilide (*Annalen*, 1895, **287**, 362), has drawn attention to the fact that, whilst the O-ethyl ethers of true oxymethylene compounds boil at higher temperatures than the substances from which they are obtained, the boiling point of O-ethyl formanilide is 82° lower than that of formanilide, a fact which lends additional weight to the supposition that the anilides (and amides) actually contain the group ·CO·NH·. The same fact is also well brought out in the subjoined table by a comparison of the boiling points of several isomeric pairs of N- and O-ethers:

	N-ethers.	O-ethers.
Acetanilide methyl	253°[1]	197°
Acetanilide ethyl	258[1]	207—208
Aceto-*o*-toluidide methyl	252	212
Aceto-*o*-toluidide ethyl	254—256[2]	222
Aceto-*p*-toluidide ethyl	258[3]	232
Oxamic ester ethyl	244—246[4]	175[5]
Urethane ethyl	175[6]	138[7]

I. Alkylation of Acetanilide.

Action of Methyl Iodide and Dry Silver Oxide on Acetanilide.

The following experiment resulted in the formation of N-phenylacetimino-methyl ether, associated, however, with a nearly equal quantity of the isomeric N-methylacetanilide.

A mixture of 46 grams of dry silver oxide with a solution of 13·5 grams of acetanilide in 57 grams of methyl iodide and 20 c.c. of benzene was boiled for 1½ hours. On distillation under 11 mm. pressure, 5 grams of a colourless, pleasant-smelling liquid boiling at 95—105°, a small fraction (0·5 gram) of rapidly rising boiling point, and thereafter a solid fraction boiling below 190°, were obtained.

The liquid fraction was divided by redistillation under atmospheric

[1] Pictet and Crépieux, *Ber.*, 1888, **21**, 1108.
[2] Reinhardt and Städel, *Ber.*, 1883, **16**, 31.
[3] Norton and Livermore, *Ber.*, 1887, **20**, 2271.
[4] Wallach, *Annalen*, 1877, **184**, 59.
[5] Nef, *Annalen*, 1895, **287**, 288.
[6] Würtz, *Jahresb.*, 1854, 565.
[7] Hantzsch and Mai, *Ber.*, 1895, **28**, 2470.

pressure into two parts boiling at 195—197° and 197—200° respectively, the latter of which was analysed:

0·1271 gave 0·3366 CO_2 and 0·0850 H_2O. C = 72·22; H = 7·43.
$C_6H_5 \cdot N{:}C(OMe) \cdot CH_3$ requires C = 72·48; H = 7·38 per cent.

The identity of the liquid with N-phenylacetimino-methyl ether was proved by its ready hydrolysis by hydrochloric acid, and by its conversion into diphenylethenylamidine (m. p. = 131—132°) on warming with aniline. Platinic chloride added to a cold, freshly prepared solution of the imino-ether in dilute hydrogen chloride caused the separation of aniline platinichloride (Pt = 32·77 per cent.).

The solid distillate fused below 100°, and after recrystallisation from benzene, and from a mixture of benzene and light petroleum, melted at 99—100°; it was identified as N-methylacetanilide.

Found C = 72·29; H = 7·42; N = 9·80.
$C_9H_{11}ON$ requires C = 72·48; H = 7·38; N = 9·39 per cent.

The simultaneous formation of both N- and O-methyl ethers in the methylation of acetanilide (compare also the case of aceto-*o*-toluidide, and of aceto-*p*-toluidide) is at first sight a somewhat puzzling phenomenon. It was thought that the difference in the action of methyl and ethyl iodides on anilide and silver oxide might be due either to the lower temperature obtaining during methylation, or to the considerably smaller solubility of the anilide in methyl iodide. The speed of reaction could scarcely determine the difference, for methyl iodide acts equally as rapidly as ethyl iodide, if not rather more rapidly than it.

A number of comparative experiments were carried out in which the conditions of reaction were made as nearly as possible alike. Addition of benzene prior to ethylation was tried, in order to examine the influence of this solvent. Other preparations were carried out in which the solubility of the anilide and the temperature of the gently boiling liquid were reduced to approximately those obtaining during methylation by addition of ether. In most cases, from 9 to 11 grams of ethyl imino-ether were obtained from 13·5 of anilide, and the small quantities of solid, obtainable by pursuing the distillation after separation of the main product, proved to be acetanilide. In every instance, a mixture of the two methyl ethers was obtained. Although N-ethyl ethers were never isolated as products of any of the alkylation experiments described in this paper, it is still possible that they may have been formed in quantities too small for detection.

A partial explanation of the anomalous reaction with methyl iodide is afforded by the fact that N-phenylacetimino-methyl ether suffers incomplete molecular rearrangement on boiling for a few hours under the atmospheric pressure.

Similar observations of the lability of alkyl groups in the enolic or O-ethers have been made in the case of imino-ethers by Wheeler and Johnson (*Ber.*, 1899, **32**, 35) and by Wislicenus and Goldschmidt (*Ber.*, 1900, **33**, 1467); in the case of phenyl vinyl ethers by Claisen (*Ber.*, 1897, **29**, 2932); and in the case of acyl groups in $\cdot CH_2 \cdot CO \cdot$ compounds by Claisen and Haase (*Ber.*, 1900, **33**, 3780) and by Wislicenus and Körber (*Ber.*, 1901, **34**, 218).

A further discussion of these interesting and theoretically significant phenomena is deferred for the present, as the author hopes to be able to carry out further experiments bearing on this point with some of the imino-ethers described in this paper.

II. *Alkylation of Aceto-o-toluidide.*

Action of Ethyl Iodide and dry Silver Oxide on Aceto-o-toluidide.

This reaction led, so far as could be ascertained, to the exclusive formation of N-*o*-tolylacetimino-ethyl ether.

A mixture of 35 grams of dry silver oxide with a solution of 15 grams of toluidide in 48 grams of ethyl iodide diluted with a little benzene was boiled for 1½ hours. On distillation under 20 mm. pressure, 14 grams of a colourless liquid boiling at 125—130° were obtained. The residue fused at 110° after recrystallisation and was unchanged aceto-*o*-toluidide. No N-ethylaceto-*o*-toluidide could be detected. The liquid imino-ether boiled at 222° under 740 mm. pressure. On analysis:

0·12 gave 8·2 c.c. moist nitrogen at 11° and 752 mm. N = 8·04.

$CH_3 \cdot C_6H_4 \cdot N{:}C(OEt) \cdot CH_3$ requires N = 7·91 per cent.

After boiling a small quantity of N-*o*-tolylacetimino-ethyl ether with moderately strong hydrochloric acid for a few seconds, addition of platinic chloride in aqueous solution precipitated a double salt containing Pt = 24·2 per cent. From a solution prepared with cold dilute acid, the same reagent precipitated the platinichloride of the imino-ether, the salt being air-dried for analysis.

0·3280 gave 0·0840 Pt. Pt = 25·61.

$(C_{11}H_{15}ON)_2,H_2PtCl_6$ requires Pt = 25·50 per cent.

The same salt melting at 171° with decomposition was also formed in a state of purity (Pt = 25·66 per cent.) when platinic chloride was added to the cold aqueous solution of the imino-hydrochloride described below. The base liberated either from the platinichloride, or from the cold, freshly prepared solution of the imino-ether in dilute hydrogen chloride by potassium hydroxide, gave no yellow coloration with hypochlorite and was therefore free from *o*-toluidine.

The hydrochloride of N-*o*-tolylacetimino-ethyl ether was precipitated as a somewhat sticky mass when a solution of hydrogen chloride in dry ether was added to a light petroleum solution of the imino-ether. Dried on a porous tile over potash, it formed a hard, white crust, softening at 89° and fusing at 90—91° with copious evolution of gas (ethyl chloride), leaving a residue of aceto-*o*-toluidide, a behaviour which is characteristic of imino-ether hydrochlorides.

As indicated above, the hydrochloride is soluble without decomposition in cold water, but a solution of the salt in undried alcohol and ether deposits *o*-toluidine hydrochloride (m. p. 211°) on prolonged standing.

Action of Methyl Iodide and dry Silver Oxide on Aceto-o-toluidide.

Methylation of aceto-*o*-toluidide by means of silver oxide and methyl iodide resulted in the formation of a mixture of both N- and O-ethers in a manner analogous to that followed in the methylation of acetanilide. It was thought probable that the relatively great stability of the *o*-tolylacetimino-ether might prevent the formation of the isomeric N-ether. Indeed, as a comparison with the methylation of aceto-*p*-toluidide shows, the pressure of the *o*-methyl group actually seems to prevent the formation of N-ether to a greater extent than the presence of a *p*-methyl group.

Thirty-four grams of dry silver oxide were added to a warm solution of 15 grams of aceto-*o*-toluidide in 42 grams of methyl iodide and 20 c.c. of benzene, and the mixture boiled for 4 hours. By two distillations under about 20 mm. pressure, the product was divided into three fractions boiling at 99—105°, 105—120°, and 120—145° respectively, and by further distillation under atmospheric pressure into a liquid fraction boiling at 210—214° which was the imino-ether, a mixed liquid fraction boiling at 214—250°, and a fraction boiling at 252° which solidified, and after drying on a porous tile melted at 55—56°. This solid was evidently N-methylaceto-*o*-toluidide which melts at 56° (Nölting, *Ber.*, 1878, **11**, 2279).

The fraction boiling at 210—214° was identified as N-*o*-tolylacetimino-methyl ether, $CH_3 \cdot C_6H_4 \cdot N{:}C(OMe) \cdot CH_3$.

0·0960 gave 6·9 c.c. moist nitrogen at 13° and 756 mm. N = 8·42.

$C_{10}H_{13}ON$ requires N = 8·58 per cent.

It showed the same relative stability towards acids as the imino-ethyl ether, and when dissolved in cold dilute hydrochloric acid gave needle-shaped crystals of the imino-platinichloride on the addition of platinic chloride; these were air-dried for analysis:

0·2760 gave 0·0740 Pt. Pt = 26·81.

$(C_{10}H_{13}ON)_2,H_2PtCl_6$ requires Pt = 26·47 per cent.

The amino-hydrochloride, prepared by the method used for the ethyl derivative (p. 694), melted with evolution of gas at 79—80°, leaving a residue of aceto-*o*-toluidide. By solution in cold water and addition of strong aqueous platinic chloride, the pure imino-platinichloride (Pt = 26·45 per cent.) was obtained; this melted at 169° with decomposition.

The relative stability of the *o*-tolylacetimino-ethers presents a case of the stereochemical hindering of reaction which, perhaps, might quite well be anticipated. V. Meyer's 'esterification law' does not, however, seem to apply to a notable extent to *o*-toluic acid, which undergoes esterification almost as readily as its *p*-isomeride.

N-*o*-tolylacetimino-ethyl ether, dissolved in cold dilute hydrochloric acid, suffers slow hydrolysis, the rapidity of development and the depth of the *o*-toluidine hypochlorite coloration increasing with time of standing.

The orientation seems also to exercise a marked influence on the formation of amidines. When 3·5 grams of N-*o*-tolylacetimino-ethyl ether were warmed for 3 hours at 90—100° with 2·1 grams of *o*- and *p*-toluidine respectively, and the products converted into hydriodides, 0·4 gram of insoluble or amidine salt was obtained from the former, and 4·1 grams, or 55 per cent., from the latter. The presence of methyl groups in the ortho-position in the imino-ether and in the amine seems to inhibit this type of condensation.

It may also be added, that whereas N-methylaceto-*p*-toluidide can be readily hydrolysed by strong caustic alkali, the *o*-isomeride, under the same conditions, is notably more stable.

As will be seen from the experiments described on p. 697, N-α-naphthylacetimino-ethyl ether is much less stable than the *o*-tolyl compound, from which it would appear that an *o*-phenylene group exercises less influence in hindering hydrolysis by acids than an *o*-methyl group.

In view of the relatively great stability of the *o*-tolylimino-ethers, it was thought that the hitherto unknown *o*-toluoimino-ether, $CH_3 \cdot C_6H_4 \cdot C(:NH) \cdot OEt$, might be prepared from *o*-toluamide by means of silver oxide and ethyl iodide, and that it would probably be an ether of the same relative stability as the N-*o*-tolylacetimino-ethers. This ether cannot be prepared from *o*-toluonitrile (Pinner, Imidoäther, 63), a failure for which stereochemical explanation at once suggests itself. Since, however, stereochemical hindering is not manifested in the process of salt formation, the ether might be expected to be formed readily by the alkylation of toluamide* in a manner analogous to that followed in the alkylation of benzamide, but experiment showed that only *o*-toluonitrile was obtained.

* The amide fused at 141°, instead of 138°, as given in the literature.

III. *Alkylation of Aceto-*p*-toluidide.*

*Action of Ethyl Iodide and Dry Silver Oxide on Aceto-*p*-toluidide.*

The ethylation was carried out by boiling together for 4 hours, 35 grams of silver oxide, 20 grams of aceto-*p*-toluidide, 48 grams of ethyl iodide, and 20 c.c. of benzene. A considerable amount of the toluidide escaped reaction; the proportion $1\frac{1}{2}$ mols. of the oxide to 1 mol. of the acetyl compound seems the most suitable. The liquid imino-ether, amounting to 12 grams, was separated from unchanged aceto-*p*-toluidide by distillation; it boiled at 125—130° under 12 mm., and at 232° under atmospheric pressure. No N-ethylaceto-*p*-toluidide could be detected.

0·1430 gave 9·9 c.c. moist nitrogen at 15° and 760 mm. N = 8·09.
$C_{11}H_{15}ON$ requires N = 7·91 per cent.

When a small quantity of this ether was dissolved in cold dilute hydrochloric acid, and platinic chloride and alcohol were at once added, *p*-toluidine platinichloride (Pt = 31·01 per cent.) was deposited.

p-Tolylacetimino-ethyl ether, unlike the ortho-compound, rapidly acquires a brown tint on keeping.

The hydrochloride also is less stable than the corresponding ortho-salt. Addition of dry ethereal hydrogen chloride to a light petroleum solution of the imino-ether precipitated a sticky mass which did not dry on prolonged standing over potash. When gently warmed on a watch glass, this substance fused, evolving gas and leaving a residue which melted at 125—135°.

*Action of Methyl Iodide and dry Silver Oxide on Aceto-*p*-toluidide.*

Under the conditions of the following experiment, only N-methylaceto-*p*-toluidide was isolated in the pure state.

Thirty-five grams of silver oxide, 15 grams of aceto-*p*-toluidide, 42 grams of methyl iodide, and 30 c.c. of benzene were boiled together for 2 hours, the initial reaction being somewhat vigorous. On distillation of the product under 15 mm. pressure, nothing came over below 165°, but 12 grams of a solid distilled at this temperature,* and on redistillation under atmospheric pressure boiled at 260—280°.

On recrystallisation from light petroleum, the solid fused at 63—65°, and after a second crystallisation at 64—66°. As the melting point of N-methylaceto-*p*-toluidide is given as 83° by Thomsen (*Ber.*, 1877, 10, 1583), the identity of the product melting at 64—66° was checked by analysis and hydrolysis.

* The first portions of the distillate being contaminated with a brown oil, which was probably the imino-ether.

0·1373 gave 10·3 c.c. moist nitrogen at 15° and 766 mm. N = 8·83.
$C_{10}H_{13}ON$ requires N = 8·58 per cent.

The base obtained by hydrolysis with strong aqueous potassium hydroxide gave a platinichloride containing Pt = 29·42, that of methyl toluidine requiring 29·88 per cent.

IV. *Alkylation of the Acetonaphthalides.*

Action of Ethyl Iodide and dry Silver Oxide on Aceto-α-naphthalide.

Thirty-five grams of dry silver oxide, and a solution of 25 grams of aceto-α-naphthalide in 48 grams of ethyl iodide, 40 c.c. of benzene, and a little alcohol, were boiled together for 3 hours. Unaltered naphthalide and N-α-naphthylacetimino-ethyl ether, $C_{10}H_7 \cdot N{:}C(OEt) \cdot CH_3$, were the only products isolated. After three distillations under reduced pressure, 15 grams of the imino-ether were obtained as a faintly yellow liquid, rapidly acquiring a red colour on keeping, and boiling at 175° under 12 mm. pressure.

0·1430 gave 8·1 c.c. moist nitrogen at 13° and 756 mm. N = 6·64.
$C_{14}H_{15}ON$ requires N = 6·57 per cent.

N-α-Naphthylacetimino-ethyl ether does not display the same relative stability as the N-*o*-tolyl compound. When platinic chloride was added to solutions of the imino-ether prepared either by warming with alcohol and dilute hydrochloride acid, or by standing with the same reagent for 24 hours, α-naphthylamine platinichloride, crystallised with $2H_2O$ in dense orange crystals which blackened and intumesced at 227°, was deposited.

0·2515 lost 0·0125 at 110° and gave 0·0670 Pt. H_2O = 4·97; Pt = 28·03.
$(C_{10}H_7 \cdot NH_2)_2, H_2PtCl_6, 2H_2O$ requires H_2O = 4·92; Pt in dry salt = 27·99 per cent.

Addition of platinic chloride to a freshly prepared acid alcoholic solution of the imino-ether, or of the hydrochloride, caused the formation of a gummy, yellow salt, which rapidly decomposed with blackening, but was probably the iminoplatinichloride.

The hydrochloride, precipitated by ethereal hydrogen chloride from a light petroleum solution of the imino-ether, and dried over potash, melted at 111°, evolving gas; it almost immediately resolidified and then fused at 150—151°.

Action of Ethyl Iodide and dry Silver Oxide on Aceto-β-naphthalide.

Thirty-five grams of silver oxide, 14 grams of aceto-β-naphthalide, 48 grams of ethyl iodide, and 10 c.c. of alcohol were boiled together

for 3 hours. The product, purified by distillation until the liquid no longer gave a turbidity with light petroleum, amounted to 7 grams of N-β-naphthylacetimino-ethyl ether, boiling at 176·5° under 12 mm. pressure.

0·1167 gave 6·8 c.c. moist nitrogen at 13° and 724 mm. N = 6·54.
$C_{14}H_{15}ON$ requires N = 6·57 per cent.

The imino-ether is a liquid of faint yellow colour when freshly distilled, and has a marked blue fluorescence. It rapidly turns dark red on keeping, and readily undergoes hydrolysis by dilute acids, giving β-naphthylamine. Platinic chloride precipitated β-naphthylamine platinichloride (Pt = 27·33 per cent.) from a cold freshly prepared solution in alcohol and dilute hydrochloric acid.

V. *Alkylation of Benzanilide.*

Action of Ethyl Iodide and dry Silver Oxide on Benzanilide.

The reaction between 29 grams of silver oxide, 19 grams of benzanilide, and 40 grams of ethyl iodide, solution of the anilide being aided by the addition of 50 c.c. of benzene, was not vigorous, but after 3 hours' boiling, about one-half of the anilide was converted into the N-phenylbenzimino-ethyl ether, $C_6H_5{\cdot}N{:}C(OEt){\cdot}C_6H_5$, previously described by Lossen (*loc. cit.*). On distillation under 100 mm. pressure, the product was obtained as an oil mixed with crystals of benzanilide. By extraction with light petroleum and two further distillations, 9 grams of a thick, slightly yellow oil were obtained boiling at 176° under 12 mm. pressure, and giving no turbidity on addition of light petroleum.

0·2270 gave 12·2 c.c. moist nitrogen at 10° and 740 mm. N = 6·25.
$C_{15}H_{15}ON$ requires N = 6·22 per cent.

This imino-ether shows very well the nature of the characteristic acid hydrolysis. When 3 grams were boiled for about 15 minutes with moderately strong hydrochloric acid, ethyl benzoate (b. p. 210°) and aniline hydrochloride were obtained, the hydrolysis being represented by the equation:

$$C_6H_5{\cdot}N{:}C(OEt){\cdot}C_6H_5 + H_2O + HCl = C_6H_5{\cdot}NH_2{,}HCl + C_6H_5{\cdot}CO_2Et.$$

The behaviour of the imino-ether towards anhydrous hydrogen chloride has been described by Lossen, who obtained the hydrochloride which on gently heating gave ethyl chloride and benzanilide.

VI. *Alkylation of Ethyl Oxanilate.*

Action of Ethyl Iodide and dry Silver Oxide on Ethyl Oxanilate.

Semi-N-phenylimino-oxalic dimethyl ether has been described by Anschütz and Stiepel (*loc. cit.*). The diethyl ether may be readily prepared from ethyl oxanilate by means of dry silver oxide and ethyl iodide.

The reaction between 35 grams of silver oxide, 19 grams of ethyl oxanilate, and 48 grams of ethyl iodide was very energetic, and the flask was therefore cooled with water. After subsequent boiling for 2 hours, the product was twice distilled under diminished pressure, when 17·5 grams were collected, boiling at 152—155° under 12 mm. pressure.

Semi-N-phenylimino-oxalic diethyl ether is a colourless liquid when distilled, but almost immediately acquires a faint yellow tint. It is readily soluble in light petroleum, and in cold dilute hydrochloric acid, being resolved thereby into aniline and oxalic acid.

0·1578 gave 8·6 c.c. moist nitrogen at 10° and 730 mm. N = 6·25.

$C_{12}H_{15}O_3N$ requires N = 6·33 per cent.

When ethereal hydrogen chloride was added to a light petroleum solution of the imino-ether, an oil separated, which on stirring soon solidified and after drying over potash partially melted at 60° but fused completely at 150°, no gas being evolved. This behaviour on heating, in all likelihood, indicates the presence of ethyl oxanilate and of anhydrous oxanilic acid, evidently arising from decomposition of the imino-hydrochloride at the ordinary temperature and partial hydrolysis of the oxanilic ester thus formed. The mother liquor poured off from the precipitated compounds deposited crystals of hydrated oxanilic acid on evaporation in the air.

Reaction between Semi-N-phenylimino-oxalic Diethyl Ether and Aniline.—The reaction between this imino-ether and aniline at 100°, which was expected to give diphenylamidino-oxalanilide described by Anschütz and Stiepel (*loc. cit.*), and earlier by Klinger (*Annalen*, 1877, **184**, 280), led to the formation of diphenylamidino-oxalic ester.

Four and a half grams of the imino-ether and 4 grams of aniline were warmed together for 3 hours in boiling water. On prolonged standing, the liquid became semi-solid through the separation of needles, which were recrystallised by solution in alcohol and addition of water until a turbidity was caused. After three recrystallisations, the compound was obtained in colourless needles, melting at 73—74° to a yellow liquid without decomposition. Solutions of the purified compound also had a yellow colour.

The amidino-ester was purified by solution in hydrogen chloride, precipitation by sodium carbonate, and recrystallisation.

0·1712 gave 15·2 c.c. moist nitrogen at 15° and 757 mm. N = 10·33.
$C_{16}H_{16}O_2N_2$ requires N = 10·44 per cent.

It dissolves easily in cold, dilute, hydrochloric acid leaving a small residue of insoluble compound (probably diphenylamidino-oxalanilide), which was removed by filtration. Addition of platinic chloride to the solution caused the separation of needle-shaped crystals of a double salt.

0·2390 gave 0·0495 Pt. Pt = 20·71.
$(C_{16}H_{16}O_2N_2)_2,H_2PtCl$ requires Pt = 20·59 per cent.

The diphenylamidino-oxalanilide described by Klinger and by Anschütz and Stiepel was easily made by warming the corresponding amidino-ester with aniline at 160—170° for 4 hours. After recrystallisation from benzene and alcohol, the product was obtained in honey-yellow crystals which softened at 124°, fused at 142°, had the same melting point after resolidification, and did not decompose at 250° (compare Anschütz and Stiepel, *loc. cit.*).

0·1443 gave 16·1 c.c. moist nitrogen at 10° and 766 mm. N = 13·44.
$C_{20}H_{17}N_3O$ requires N = 13·33 per cent.

VII. *Alkylation of Oxanilide.*

Action of Ethyl Iodide and dry Silver Oxide on Oxanilide.

The reaction between 46 grams of dry silver oxide, 18 grams of oxanilide, and 63 grams of ethyl iodide dissolved in 50 c.c. of benzene was tardy, owing to the sparing solubility of the anilide. After 3 hours' boiling, most of the anilide had passed into solution, a very moderate reaction having occurred at the outset. After two distillations, 8·5 grams of di-N-phenylimino-oxalic diethyl ether, $(C_6H_5{\cdot}N{:}COEt)_2$, were obtained, boiling at about 205° under 12 mm. pressure. It was a viscid liquid of rather dark brown colour.

0·1220 gave 9·5 c.c. moist nitrogen at 10° and 760 mm. N = 9·30.
$C_{18}H_{20}O_2N_2$ requires N = 9·46 per cent.

On boiling some of the imino-ether with strong hydrochloric acid, a small amount of a gummy solid, which probably contained oxanilide, was formed; the acid solution contained oxalic acid and aniline.

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LXXVII.—*Preparation of Aliphatic Imino-ethers from Amides.*

By G. Druce Lander.

As is well known, Pinner's imino-ethers are alkyl ethers of the acid amides, corresponding to the labile or enolic form, ·C(OH):NH, of the amido-group, ·CO·NH_2. So far, the weight of evidence, for example, that of the boiling points of the isomeric O- and N-ethers (this vol., p. 691), tends to prove that in the free state the amides do not possess the enolic structure. In this connection, however, it is interesting to note that molecular conductivity determinations of acetamide and benzamide quoted by Titherley (Trans., 1901, 79, 410) show that there is apparently a greater tendency on the part of benzamide to undergo dissociation in dilute aqueous solution than is the case with acetamide, and this observation harmonises with the fact that silver benzamide reacts as if it contained the radicle OAg, whereas silver acetamide, under the same circumstances, does not (Tafel and Enoch, *Ber.*, 1890, 23, 103, 1550). The transformation of imino-ether hydrochlorides into amides by loss of alkyl chloride on heating is a general reaction, characteristic also of N-substituted imino-ethers, which serves to link together these two classes of amides.

In the study of alkylation by means of silver oxide, the author's attention has been largely directed to the possibility of effecting syntheses of aliphatic imino-ethers from amides by the use of dry silver oxide and ethyl iodide.

The employment of this reagent obviates the necessity for isolating any silver salt in the free state, and is capable of better regulation than is likely to be possible when a silver salt is allowed to act on an alkyl iodide.

The somewhat fugitive nature of aliphatic imino-ethers, as evidenced by their frequent decomposition on liberation from the hydrochlorides by alkali, the polymeric or other changes occasionally undergone on heating, and the very great susceptibility of their hydrochlorides to decomposition by water, greatly tends to render their isolation and certain detection a matter of some difficulty. Indeed, the author's experience in great measure confirms Tafel and Enoch's remark as to the difference in the behaviour of aliphatic as compared with aromatic amides.

The results of a study of ethyl oxamate, urethane, and acetamide are described in the present paper.

Preparation of Semi-imino-oxalic Diethyl Ether from Ethyl Oxamate.

This imino-ether has been described by Nef (*Annalen*, 1895, **287**, 288), who prepared it by the partial hydrolysis of diimino-oxalic ether by dilute hydrochloric acid, the yield amounting to 8 grams from 48 grams of the di-ether. He also obtained the chloride by the addition of alcohol by the aid of hydrogen chloride to ethyl cyanocarbonate.

The imino-ether can be easily prepared from ethyl oxamate by means of dry silver oxide and ethyl iodide. A very vigorous reaction occurred when 46 grams of oxide and a solution of 17 grams of oxamate in 63 grams of iodide was warmed. The mixture was diluted with ether and gently boiled for 1 hour. On distillation in a partial vacuum, a limpid, colourless liquid of pungent odour passed over below 80°, leaving much unchanged oxamate in the distilling flask. This liquid gave a crystalline hydrochloride in dry ethereal solution, from which strong alkali liberated a pungent oil; this was rapidly decomposed on exposure to air, forming ammonium chloride. The greater part was redistilled, whereby 4 grams boiling at 75—77° under a pressure of about 25 mm. were collected. Nef gives the boiling point as 73° under 18 mm. pressure. This liquid was the expected semi-imino-oxalic diethyl ether, $C{:}NH(OEt)\cdot CO_2Et$.

0·2823 gave 24·3 c.c. moist nitrogen at 10° and 730 mm. N = 9·87.
$C_6H_{11}O_3N$ requires N = 9·65 per cent.

Like Nef's compound, the imino-ether thus prepared is fairly soluble in water, and acquires a brown tint on keeping. It is completely hydrolysed by dilute hydrogen chloride, 0·325 gram giving 0·464 gram of ammonium platinichloride instead of 0·497 gram, the calculated quantity.

Preparation of Iminocarbonic Diethyl Ether from Urethane.

This imino-ether can be prepared by the action of chloro- or bromo-cyanogen on sodium ethoxide in the presence of alcohol, or on aqueous alcoholic caustic alkali solutions (Nef, *loc. cit.*, 314; Hantzsch and Mai, *Ber.*, 1895, **28**, 2470), and is the ethyl ether of the enolic form of urethane.

Sandmeyer (*Ber.*, 1886, **19**, 864) states that the imino-ether forms a hydrochloride which decomposes at the ordinary temperature into urethane and ethyl chloride.

So far as the author is aware, no attempts have previously been made to synthesise the compound from urethane. Hantzsch and Mai (*loc. cit.*, 977) describe experiments to prepare silver phenylurethane, which resulted in the formation of silver oxide.

The first experiments on the alkylation of urethane were carried out at the temperature of the steam bath. The reaction caused by the addition of the dry oxide was most energetic, and, unless carefully regulated, white fumes were evolved, a sublimate formed in the condenser, and a red litmus paper at the top of the condenser was turned blue. The liquid product boiled at 90—200°, a fairly large distillate being gathered between 170° and 180°. This fraction may have contained ethylurethane (b. p. 175°), but estimation of nitrogen gave N = 13·18 instead of 11·96 per cent. Ponomareff (*Ber.*, 1882, **15**, 515) obtained what appears to have been a similar mixture boiling at 90—200° by the action of bromocyanogen on sodium ethoxide (compare Nef, *loc. cit.*, 312).

By pursuing the distillation beyond 200°, ethyl *iso*cyanurate melting at 93—94° was obtained (N = 19·88 instead of 19·71 per cent.). It was probably formed by the decomposition of the iminocarbonic ether, which although when pure can be heated to 200° without change (Hantzsch and Mai, *loc. cit.*), may possibly at the moment of formation more easily undergo the necessary loss of alcohol, polymerisation, and molecular rearrangement. It is also not unlikely that cyanic acid might be formed by dehydration of the urethane and then by energetic alkylation give the *iso*cyanurate.

The desired imino-ether was eventually obtained by allowing a mixture of 46 grams of dry silver oxide and a solution of 18 grams of urethane in 64 grams of ethyl iodide and 50 c.c. of dry ether to stand with occasional shaking for 10 days at the temperature of the laboratory. On distillation, 2—3 c.c. of a pungent liquid passed over at 75—80° under a pressure of 20—30 mm., leaving a residue of unchanged urethane and a small quantity of liquid.

The liquid distillate was allowed to stand over concentrated aqueous potassium hydroxide for a week, separated, diluted with ether, and dehydrated by solid potash. The product was converted into the bromoimino-ether in which bromine can be estimated iodometrically (Hantzsch and Mai). By running dilute potassium hypobromite solution into the aqueous solution of about 0·5 gram of the imino-ether, about 0·4 gram of bromoiminocarbonic diethyl ether was obtained, melting after crystallisation from ether, at 40—42°, instead of at 43°.

0·1643 required 16·65 c.c. N/10 thiosulphate. Br = 40·5.
0·1327 „ 13·45 c.c. „ Br = 40·5.
$C_5H_{10}O_2NBr$ requires Br = 40·8 per cent.

Experiments with Acetamide.

In spite of several experiments carried out both in the cold and at the temperature of the steam-bath, the formation of acetimino-ethyl

ether from acetamide by the action of silver oxide and ethyl iodide could not be demonstrated.

When carried out at 100°, energetic action set in, accompanied apparently by more or less profound decomposition, as no pure product could be isolated from the resulting mixtures.

In the cold, the mixture acquired a distinct imino-odour, and after several weeks much acetamide remained unchanged. On distillation, a basic liquid passed over between 70° and 100°, from which only an oily, unstable hydrochloride could be prepared. Possibly it was acetimino-ethyl ether mixed with alcohol and ethyl iodide.

It may be remarked that, in the experiments carried out in the cold, no evidence of the formation of ethylacetamide was obtained.

Much of the expense incurred during the work described in this and the preceding paper was defrayed by a grant from the Research Fund of the Chemical Society, for which the author desires to express his indebtedness.

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LXXVIII.—*Preparation of Synthetical Glucosides. II.*

By Hugh Ryan, M.A., D.Sc., and W. Sloan Mills, M.A.

It has been found by one of us (Ryan, Trans., 1899, **75**, 1057) that acetyl chloride reacts with dry galactose in a manner analogous to its action on glucose (Colley, *Ann. Chim. Phys.*, 1870, [iv], **21**, 363). The compound formed by the interaction was obtained as a colourless syrup containing chlorine, and was converted into a galactoside resembling somewhat the naphthylglucoside prepared from acetylchloroglucose.

As the study of acetylchlorogalactose has since been taken up by Emil Fischer and E. F. Armstrong (*Sitzungsber. Akad. Wiss. Berlin*, 1901, 123), we find it necessary to communicate the results which we have already obtained, although our experiments with the substance are not yet completed.

Acetylchlorogalactose was prepared by the action of 56 grams of acetyl chloride on 24 grams of dry galactose in a cool, well-dried, sealed tube; much hydrogen chloride was formed in the process. The product was extracted with chloroform, and from the solution, by evaporation, a faint yellow, semi-solid syrup was obtained, which was sparingly soluble in cold alcohol and contained Cl = 6·1 per cent. instead of 9·68 per cent., showing that it was impure. Since these

experiments were made, Fischer and Armstrong (*loc. cit.*) by a different method have obtained acetylchlorogalactose in a crystalline state.

α-Naphthylgalactoside, $C_6H_{11}O_5 \cdot O \cdot C_{10}H_7$, was obtained by the action of 18·2 grams of acetylchlorogalactose, dissolved in cold absolute alcohol on a solution of 7·2 grams of α-naphthol and 2·8 grams of potassium hydroxide in about 100 c.c. of cold absolute alcohol. After remaining in a freezing mixture for twelve hours, it was allowed to stand at the temperature of the laboratory for three days, by which time the colour of the solution was brown, and a considerable quantity of solid had separated. The solution smelt of ethyl acetate; it was boiled for two hours under a reflux condenser and filtered while hot from a residue of potassium chloride. The filtrate evaporated on the water-bath gave a syrupy residue, which crystallised after standing for five days. The substance was washed free from α-naphthol by ether and recrystallised from alcohol. It was dried in the air at 105° and melted at 202—203°.

0·1078 gave 0·2471 CO_2 and 0·0572 H_2O. C = 62·51; H = 5·9.
$C_{16}H_{18}O_6$ requires C = 62·74; H = 5·88 per cent.

α-Naphthylgalactoside crystallises in rectangular plates soluble in hot alcohol or hot water, slightly so in cold water, but insoluble in ether, chloroform, benzene, or ethyl acetate. It has scarcely any action on Fehling's solution, even on continued boiling, but reduces it readily after hydrolysis by dilute sulphuric acid. It is not more soluble in dilute potash than in water, and therefore does not contain an unchanged phenolic hydroxyl group.

In a similar manner to that described for β-naphthylglucoside (Trans., 1899, **75**, 1057) we obtained *m*-cresylglucoside, $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH_3$. Molecular quantities of acetylchloroglucose, *m*-cresol, and potash dissolved in absolute alcohol were mixed together and cooled in a freezing mixture. Potassium chloride separated out from the solution, which was then heated on the water-bath and filtered. By the spontaneous evaporation of the solvent the glucoside crystallised out; it was recrystallised from 60 per cent. alcohol, dried at 105°, and then melted at 167·5—168·5°.

0·2004 gave 0·4239 CO_2 and 0·1181 H_2O. C = 57·63; H = 6·55.
$C_{13}H_{18}O_6$ requires C = 57·77; H = 6·7 per cent.

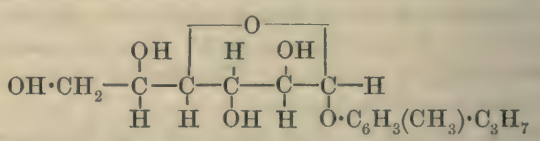
m-Cresylglucoside crystallises in long, silky, branching needles. It is scarcely soluble in benzene, chloroform, ethyl acetate, or carbon disulphide, but dissolves in cold water or in alcohol. Fehling's solution is reduced only after hydrolysis of the glucoside by dilute acids.

In addition to acetylchloroglucose and acetylchlorogalactose, the acetylbromoglucose discovered by Königs can be used with success in

the synthesis of phenolic glucosides. As the bromo-derivative is easily obtained in a crystalline form, it is a very convenient agent for the synthesis of glucosides, and Königs has shown that it is easily converted by alcohols of the fatty series into the corresponding glucosides. We have found that the crystalline bromo-compound reacts even more readily than the syrupy chloro-derivative with carvacrol in alkaline solution, giving the well crystallised carvacrylglucoside already obtained by one of us from acetylchloroglucose.

Two grams of acetylbromoglucose prepared from acetyl bromide and glucose by the method described for acetylchlorogalactose were added to a cooled solution of 0·7 gram of carvacrol and 0·3 gram of potash in absolute alcohol. A solid, which was afterwards found to be potassium bromide, separated very slowly. The mixture was boiled and filtered, and on the spontaneous evaporation of the filtrate, a yellow oil remained which crystallised after a few days. It was recrystallised from hot water, and agreed in properties with the carvacrylglucoside obtained from acetylchloroglucose.

Carvacrylglucoside is readily soluble in dilute or concentrated alkali, and is reprecipitated *unchanged*, not only by dilute acids, but by ammonium carbonate. Hence it contains an unchanged phenolic hydroxyl group, and is the first member of a hitherto unknown series of glucosides. Its formula is :



if we assume the formula for the β-glucosides attributed to them by Emil Fischer.

Addendum.—Although the crystalline acetylchloroglucoses and acetylchlorogalactoses cannot be easily obtained by the action of acetyl chloride on glucose or galactose in an open or closed vessel, a well crystallised triacetylchloroarabinose is formed by the action of acetyl chloride on well-dried arabinose in a closed *or* an open vessel. The substance is much more stable in moist air than the corresponding glucose compounds, and when recrystallised from ethyl acetate melts at 150—152°. It was dried in the air at 100—105° for analysis :

0·1532 gave 0·0741 AgCl. Cl = 11·94.

$C_{11}H_{15}O_7Cl$ requires Cl = 12·02 per cent.

Triacetylchloroarabinose, $OAc\cdot CH_2\cdot CH\cdot CH(OAc)\cdot CH(OAc)\cdot CHCl$, is

soluble in alcohol, ether, benzene, chloroform, or ethyl acetate, but

very sparingly so in hot water. It reduces Fehling's solution and crystallises in doubly refractive prisms. By the action of hot methyl alcohol it is converted into a crystalline arabinoside which seems to be identical with that obtained from arabinose and methyl alcohol by Emil Fischer's excellent method.

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LXXIX.—*The Influence of Cane Sugar on the Conductivities of Solutions of Potassium Chloride, Hydrogen Chloride, and Potassium Hydroxide, with Evidence of Salt Formation in the last Case.*

By C. J. Martin, M.B., D.Sc., and Orme Masson, M.A., D.Sc.

The experiments described in this paper were undertaken in connection with a more extended inquiry concerning the power to take part in electrolytic conduction which characterises certain complex substances usually regarded as typical non-electrolytes.

It was expected that the conductivity of solutions of potash containing cane sugar would afford evidence of the formation of sucric ions (potassium sucrate), besides showing a reduction due to increased viscosity, but that the latter effect alone would be noticeable in the cases of potassium chloride and hydrochloric acid, where no chemical action with the sugar seemed likely to occur, inversion being guarded against by the use of fresh solutions prepared in the cold. These expectations were justified by the results.

It is well known that sucrates ($C_{12}H_{21}O_{11}K$ and similar compounds) may be prepared in the solid state. If they can exist in solution and act as electrolytic conductors, sugar itself must be regarded, not as a non-electrolyte, but as an acid of extremely small ionisation coefficient, capable of yielding negative ions under the influence of strong positive ones. The salt of such a weak acid, however, should be hydrolysable, tending to partial decomposition in aqueous solution in consequence of the reversibility of the action $C_{12}H_{21}O_{11}H + KOH \rightleftarrows C_{12}H_{21}O_{11}K + H_2O$. This hydrolytic decomposition of the sucrate should, however, be prevented by the addition to the solution of a sufficiently large excess of sugar, in accordance with the law of mass action which has been proved in similar instances. In other words, a strong solution of sugar should be capable of converting the whole of a small quantity of added potash into potassium sucrate. On the justifiable assumption

of complete ionisation of the potassium, such an action may be written

$$x\mathrm{C_{12}H_{22}O_{11}} + \mathrm{K^{\cdot}} + \mathrm{OH'} = \mathrm{C_{12}H_{21}O'_{11}} + \mathrm{K^{\cdot}} + \mathrm{H_2O} + (x-1)\mathrm{C_{12}H_{22}O_{11}}.$$

Under these conditions, the molecular conductivity of the solution should represent the sum of the velocities of K and the sucric ion, but modified by the viscosity effect of the extra sugar.

The solutions of potassium chloride and hydrogen chloride with sugar should, on the other hand, contain no sucric ions and should possess the conductivities of potassium chloride and hydrogen chloride modified only by the extra viscosity. The study of these cases should help to elucidate the more complicated case of potassium hydroxide and sugar by affording data for the elimination from it of the viscosity effect with, at any rate, approximate accuracy. Any residual effect should be due to the displacement, partial or complete, of hydroxyl by sucric ions.

The nature of the simple viscosity effect was investigated by Arrhenius (*Zeit. physikal. Chem.*, 1892, **9**, 487), who studied the conductivity of solutions of acids, alkalis, and salts containing such non-electrolytes as alcohols, ether, acetone, and cane-sugar, but omitted solutions of alkali and sugar. He found that, if moderate concentrations of the non-electrolyte be employed, the results can be expressed by the formula $l = l_0(1 - \alpha x)$, where l is the conductivity of the solution, l_0 that of a pure aqueous solution of the same electrolyte, x is the volume per cent. of the given non-electrolyte, and α is a constant. The value of α is dependent mainly on the non-electrolyte, varying only to a small extent with change in kind or quantity of the electrolyte. It has almost the same value in the cases of potassium hydroxide and hydrogen chloride, but slightly higher values for salts. With greater concentration of the non-electrolyte, the equation becomes $l = l_0(1 - \alpha/2x)^2$. Both expressions are derived from the interpolation formula $l = l_0(1 - \alpha x + \beta x^2 + \cdots)$ by neglecting insignificant terms; for Arrhenius found that $\beta = \alpha^2/4$.

For our purpose, it is more convenient to express the sugar concentrations in gram-molecules per litre (N). The actual strengths employed ranged up to $N = 2$, or 684 grams of sugar per litre. Such a solution is a very viscous syrup. The strength with respect to electrolyte was decinormal or less. The resistances were measured by Kohlrausch's method at a temperature of 18°, and the specific conductivities were deduced in the usual manner by correcting for the cell capacity. The values (λ) given in the following tables are the specific conductivities in reciprocal ohms multiplied by 10^4.

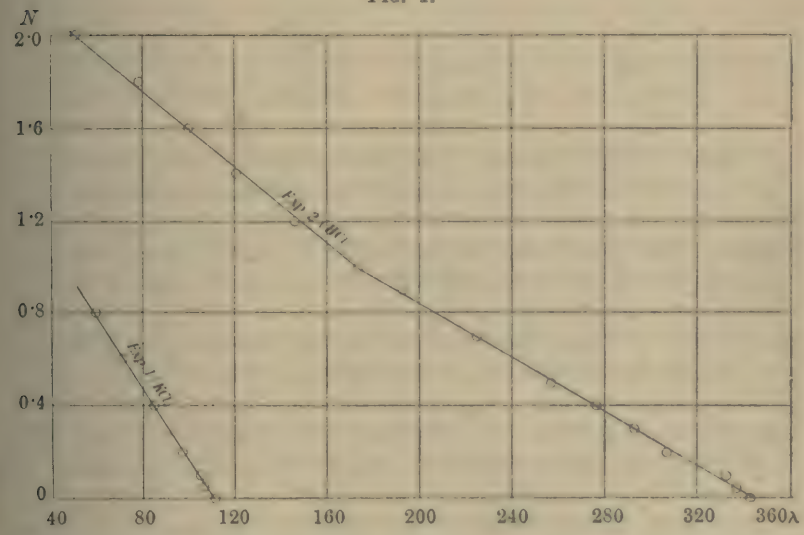
Expt. I.—Solutions of potassium chloride and sugar; the former constant in amount, the latter varying.

Gram-molecules per litre of KCl (n) = 0·1.
" " " sugar = N.

N.	λ.	110·8(1 − 0·5860N).	Difference.
0	111·4	110·8	+0·6
0·05	106·2	107·6	−1·4
0·1	105·2	104·3	+0·9
0·2	96·6	97·8	−1·2
0·4	84·8	84·8	0
0·6	71·1	71·8	−0·7
0·8	60·1	58·9	+1·2

The curve (Fig. 1) for the values of λ and N is nearly a straight line. There is here no reason to suspect chemical action, and the

FIG. 1.



reduction of the conductivity may be ascribed wholly to increased viscosity. In the third column are given calculated values which show that, within the given limits of N, λ may be obtained with a fair approach to accuracy by a simple formula resembling that used by Arrhenius. The value found for the constant α (0·586) is, however, somewhat less than that obtained by Arrhenius for 1/80 normal potassium chloride containing sugar up to 50 grams per litre; for the latter, if we translate volume per cents. into N, was 0·634.

Expt. II.—Solutions of hydrogen chloride and sugar; the former constant in amount, the latter varying.

Gram-molecules per litre of HCl (n) = 0·1.
" " " sugar = N.

N.	λ.	346 (1 − 0·5N).	Difference.
0	343	346	− 3
0·05	337	337	0
0·1	333	329	+ 4
0·2	307	311	− 4
0·3	293	294	− 1
0·4	277	277	0
0·5	257	260	− 3
0 7	225	225	0
0·9	193	190	+ 3
1·0	174	173	+ 1
1·2	146	(138)	
1·4	121	(104)	
1·6	100	(69)	
1·8	78	(35)	
2·0	51	(0)	

The curve (Fig. 1) is practically a straight line up to about $N = 1$, and the calculated values given in the third column agree with those observed for λ within this limit, but not for greater sugar concentration. The value found for the constant α (0·5) agrees well with those given by Arrhenius for 1/2 1/20, and 1/100 N hydrochloric acid containing sugar up to 50 grams per litre (or 3·14 volume per cents.); for these, when corrected so as to refer to gram-molecules per litre, become respectively 0·528, 0·509, and 0·477.

In the next experiment, a series of solutions was employed in which the concentration varied for both acid (n) and sugar (N), but a constant ratio was maintained between them. In these circumstances, it was expected that the conductivity would be found (very approximately) proportional to $N(1 - \alpha N)$, for λ/n undergoes only slight change in sufficiently dilute aqueous solutions and n may be here replaced by N, of which it is a constant fraction. But $N(1 - \alpha N)$ must obtain its maximum value when it $= 1/4\alpha$ and $N = 1/2\alpha$. If then the formula were valid and α had the value found in Expt. II for decinormal acid ($\alpha = 0{\cdot}5$), the maximum conductivity should be reached at, or close to, $N = 1$.

Expt. III.—Solutions of hydrogen chloride and sugar; both varying in concentration, but in constant ratio (1 : 20) to one another.

Gram-molecules per litre of HCl = n.
" " " sugar = N.

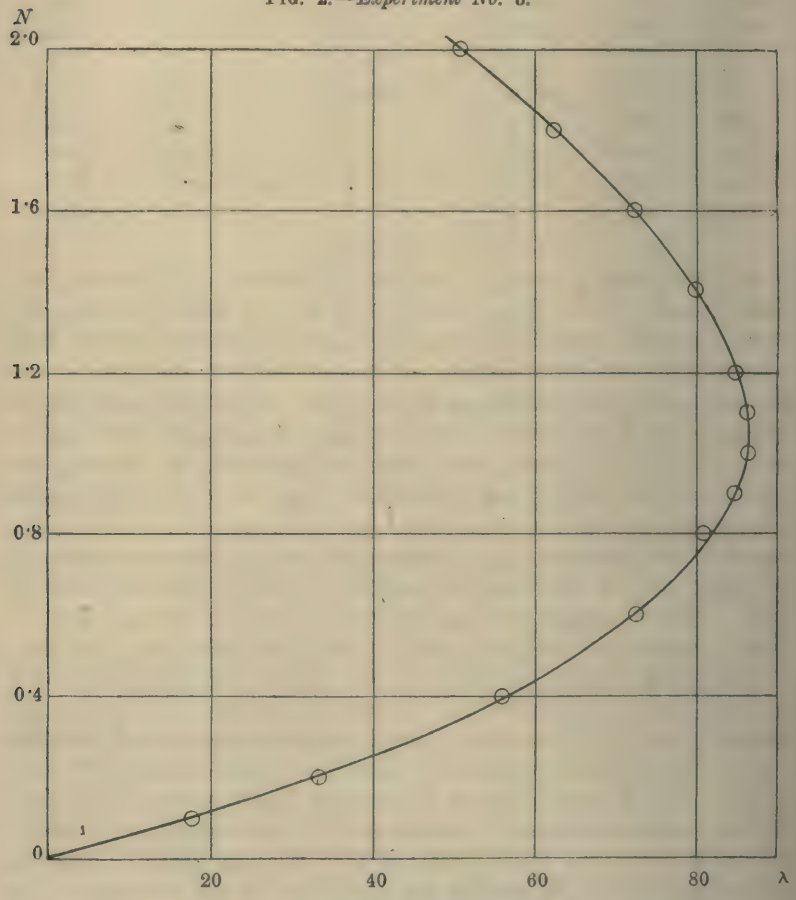
n.	N.	λ.	$3680n(1-0{\cdot}315N)^2$.	Difference.	λ/n.
0·10	2·0	50·6	50·4	+0·2	506
0·09	1·8	62·3	62·1	+0·2	692
0·08	1·6	72·2	72·6	−0·4	903
0·07	1·4	79·8	80·6	−0·8	1140
0·06	1·2	84·8	85·4	−0·6	1410
0·055	1·1	86·4	86·5	−0·1	1570
0·05	1·0	86·4	86·4	0	1730
0·045	0·9	84·8	85·0	−0·2	1880
0·04	0·8	80·9	82·4	−1·5	2020
0·03	0·6	72·5	72·6	−0·1	2420
0·02	0·4	56·0	56·2	−0·2	2800
0·01	0·2	33·1	32·3	+0·8	3310
0·005	0·1	17·7	17·3	+0·4	3540

As anticipated, a maximum of conductivity is found close to the concentration $N=1$. The curve (Fig. 2, p. 712) which expresses the results is a very symmetrical one, and shows this maximum at $N=1{\cdot}05$ ($n=0{\cdot}0525$). Its form may be ascribed to the fact that two simultaneous and opposed tendencies are at work. In the first place, dilution increases the conductivity by diminishing the viscosity of the liquid, and in the second, dilution diminishes the conductivity by lessening the amount of electrolyte in unit volume; of these, the former effect is the more potent at first, whilst the latter gains the mastery later on. The experimental results are very fairly reproduced by the figures given in the third column, which are calculated by the formula placed at its head. This is of the same form as that indicated by Arrhenius for a case of largely varying concentration of the non-electrolyte. It points to a maximum conductivity of 86·53 when $N=1/(3\times 0{\cdot}315)=1{\cdot}058$. The constant 3680 may be taken as the limiting value of the molecular conductivity, λ/n, for pure aqueous hydrochloric acid at extreme dilution, 3672 being Kohlrausch's maximum value (at $n=0{\cdot}001$ and 0·002). If it were not for the presence of sugar, causing viscosity, this molecular conductivity should vary only between 3680 and 3430, the value for the decinormal acid; so that the large viscosity effect is well shown by the figures for λ/n given in the last column of the table and reproduced in the curve of Fig. 3, *A*. For comparison, the curve for pure hydrochloric acid solution is drawn alongside (Fig. 3, *B*, p. 713).

It is worthy of note that the experimental curve (Fig. 2) is very similar in form to those which may be drawn to represent Kohlrausch's specific conductivities of pure aqueous solutions of freely soluble salts, such as lithium chloride. In all cases where the solubility is great

enough to admit of it, these curves pass through maxima of conductivity; and there is no doubt that here the true explanation is similar to that given above. But whilst the viscosity in these cases is due entirely to the electrolyte itself and is therefore small and inconspicuous except in strong solutions, in our experiment it is enormously exaggerated

FIG. 2.—*Experiment No. 3.*



by the importation of a definite large quantity of sugar with each molecule of electrolyte.

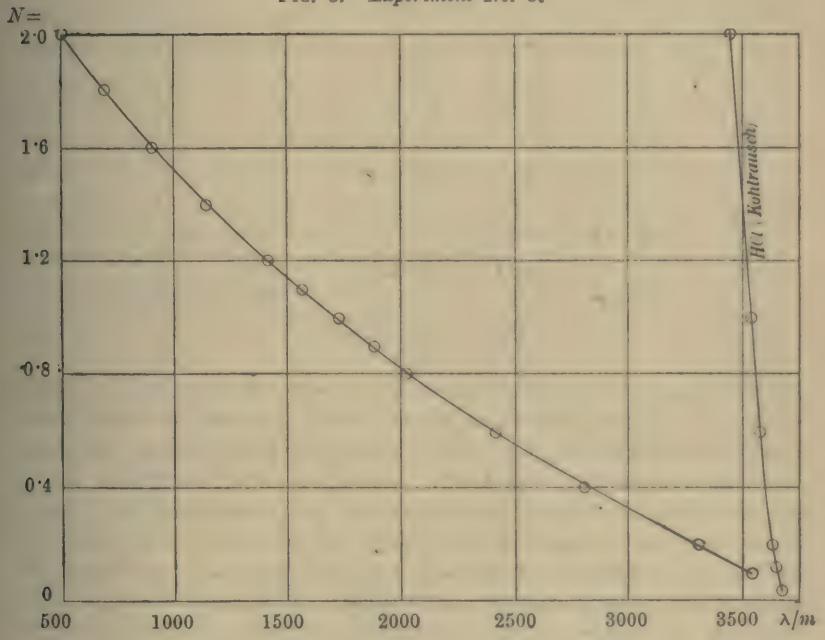
Expt. IV. Solutions of potassium hydroxide and sugar; the former constant in amount, the latter varying.

Gram-molecules per litre of KOH (n) = 0·1.

„ „ „ „ „ sugar = N.

N.	λ.	$\lambda' = \lambda/(1 - 0{\cdot}5N)$.
0·9	40·5	73·6
0·7	49·3	75·8
0·5	61·3	81·7
0·4	70·9	88·6
0·3	80·1	94·2
0·2	96·9	108
0·15	108	117
0·1	125	132
0·075	143	149
0·05	155	159
0·025	176	178
0	206	206

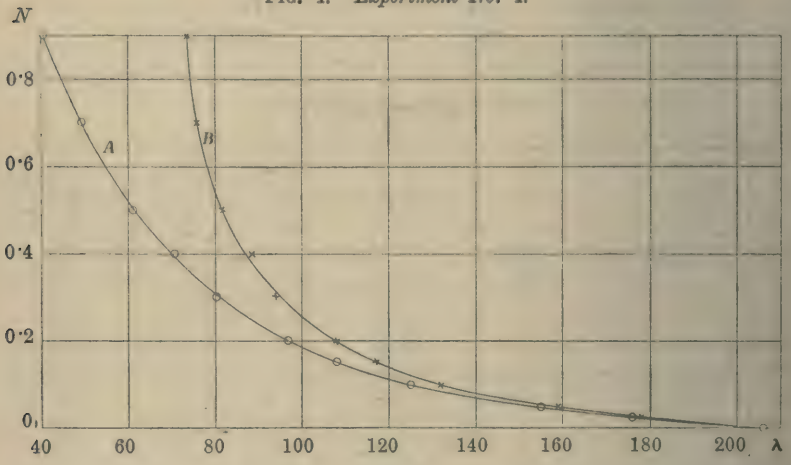
FIG. 3.—*Experiment No. 3.*



The curve illustrating this experiment (Fig. 4, *A*, p. 714) is totally different in character from those of the similar experiments with potassium chloride and hydrogen chloride. Here we have, not only a viscosity effect, but also the larger result of salt formation to reckon with. In the presence of a sufficient excess of sugar, the whole of the potassium hydroxide should be converted into sucrate or its ions, as already explained, and then, except for viscosity change, further addition of

sugar should not further reduce the conductivity. An attempt to subtract approximately the viscosity effect is shown in the figures given in the third column, the formula which proved good in the case of similar concentrations of hydrogen chloride and sugar (Expt. II) being adopted for the purpose. This proceeding is justified by the fact that Arrhenius (*loc. cit.*) found that potassium hydroxide and hydrogen chloride give very nearly the same values for the constant α in those cases where the added non-electrolyte (ethyl or *iso*propyl alcohol) does not produce chemical change, and that in general the values of α for

FIG. 4.—*Experiment No.* 4.



different electrolytes maintain about the same ratio to one another, whatever non-electrolyte be employed. The viscosity-free curve thus obtained is drawn in Fig. 4, *B*. It shows clearly enough that the corrected conductivity does tend to reach a minimum value when the sugar is present in sufficient excess to prevent hydrolysis. There is, however, too much uncertainty about the exact numerical value of the viscosity correction to warrant any inferences, such as might be drawn if this were accurately determined, concerning the true conductivity of potassium sucrate and the course of its hydrolytic decomposition.

UNIVERSITY OF MELBOURNE.

LXXX.—*A Modification of Gutzeit's Test for Arsenic.*

By Edwin Dowzard.

The subject of arsenic testing has recently received great attention, owing to the detection of that element in sodium phosphate, beer, glucose, invert sugar, &c., in fact it might be considered a distinct branch of analytical chemistry and labelled "Arsenology."

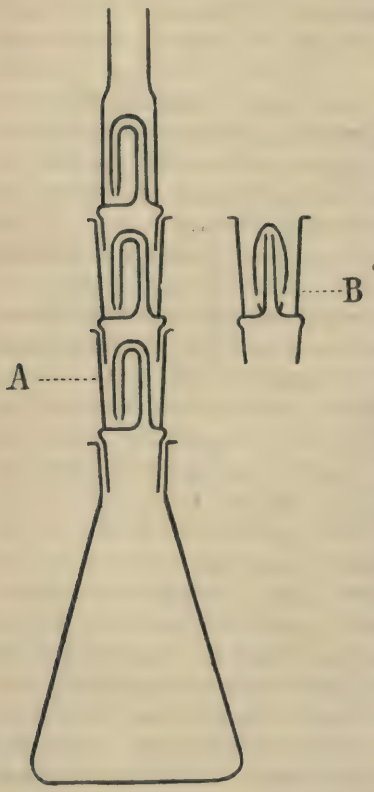
The methods which have been most used are Reinsch's, Marsh's and Gutzeit's; the first has been adopted as the official method, the second and last are also used by a number of analysts. Although Gutzeit's test is more delicate than the other two, it is open to the objection that sulphuretted hydrogen has a similar action to arseniuretted hydrogen. As the method is a most convenient one, and is also the best for quantitatively determining minute traces of arsenic, the writer has endeavoured to make it trustworthy in its indications.

Soon after the discovery of arsenic in glucose, I found that sulphuretted hydrogen could be separated from arseniuretted hydrogen by passing the mixed gases over lead acetate solution; this was effected by placing a roll of filtering paper saturated with lead acetate solution in the neck of the flask (*Chemist and Druggist*, 1900, 57, 921). A piece of apparatus has since been described for washing the gas with lead acetate solution; it is, however, too fragile for regular laboratory use. The accompanying sketch (p. 716) is that of an apparatus which the writer has designed for a similar purpose; it will be seen that the apparatus is free from a complicated system of glass bulbs and tubing, the washing cells are also easily filled and cleaned, and the gas may be washed once, twice, or thrice as desired. The cells may be obtained in two forms, A and B, from Messrs Gallenkamp and Co. of London.

The apparatus is used as follows. A weighed or measured portion of the sample is mixed with 5 c.c. of pure hydrochloric acid (if the sample is alkaline, it must be neutralised first), four drops of a 15 per cent. solution of cuprous chloride in hydrochloric acid are then added, and the mixture made up to 30 c.c. with water; if it is not convenient to work with such a small bulk as 30 c.c., this quantity may be doubled or trebled, but the same proportion of acid should be used. A rod of pure zinc, 3 cm. long and 5 mm. in diameter, is placed in the flask, the above mixture is then introduced, and the first cell placed in position; lead acetate solution (5 per cent.) is now poured into the cell until it is about half full, the second and third cells are filled in a similar manner, a small tuft of cotton wool is introduced into the neck of the top cell, and its mouth capped with mercuric chloride paper, which may be held in position by an elastic band, or a glass collar

made from a piece of glass tubing. After 40 minutes or more, the cap is removed and examined in full daylight. A minute trace of arsenic is indicated by a lemon-yellow spot, which varies in tint according to the amount present, and a heavy trace by an orange-brown spot.

The mercuric chloride paper is prepared as follows. One drop of a 5 per cent. solution of mercuric chloride is allowed to fall on the centre of a piece (4 cm. square) of thin, Swedish filtering paper such as Muncktell's No 1 F; the paper is dried before using.



The following experiments were tried with this apparatus.

(1) 0·2 gram of sodium sulphite was placed in the flask, a piece of pure zinc and 30 c.c. of dilute hydrochloric acid were introduced, and the cells placed in position as described above; after 40 minutes, the solution of lead acetate in the two lower cells was black owing to suspended lead sulphide, but the solution in the top cell was not affected; the mercuric chloride cap was colourless.

(2) 0·2 gram of sodium hypophosphite was treated in the same manner; the mercuric chloride cap was stained yellow, proving that lead acetate solution does not absorb phosphuretted hydrogen to any extent.

(3) 0·2 gram of sodium hypophosphite was treated as before, the gas being washed three times with a 15 per cent. solution of cuprous chloride in hydrochloric acid; the mercuric chloride cap was colourless. The same result was obtained when only one cell was charged with this solution, the other two remaining empty.

(4) A mixture of 0·2 gram of sodium sulphite, and 0·2 gram of sodium hypophosphite was treated as before, the gas being washed twice with cuprous chloride solution; the mercuric chloride cap was colourless.

(5) 0·000005 gram ($\frac{1}{200}$ milligram) of arsenious acid was treated in the same way, the gas being washed twice with cuprous chloride solution; the mercuric chloride cap was stained a faint yellow colour.

(6) 0·000005 gram of arsenious acid was treated as before, all the cells being empty; the mercuric chloride cap had the same yellow tint as in the previous experiment.

These experiments prove that both sulphuretted hydrogen and phosphuretted hydrogen are completely absorbed by cuprous chloride solution, whilst arseniuretted hydrogen is not affected. Lead acetate is of no use in the presence of phosphites or hypophosphites.

Experiments were tried using respectively 0·01, 0·02, 0·03, 0·04, 0·05 and 0·10 gram of potassium antimony tartrate, the gas being washed three times with cuprous chloride solution. In no case was the mercuric chloride cap stained, a faint blackish-brown stain was, however, produced by 0·2 gram.

When this modification of the Gutzeit test is used, arsenic can be detected in presence of about 2500 times its weight of antimony; in any case, antimony cannot be mistaken for arsenic, because the stain produced by antimoniuretted hydrogen has a blackish-brown colour, whilst that produced by arseniuretted hydrogen has a lemon-yellow to an orange-brown colour. Lead acetate solution does not absorb antimoniuretted hydrogen.

When antimony is present, the proportion of hydrochloric acid used should be 1 in 8, and only one drop of cuprous chloride solution should be added; this is to prevent the hydrogen from being evolved too rapidly, and to allow the cuprous chloride to exert its full absorbing power.

Selenium and tellurium compounds do not interfere with this method.

When a comparatively large amount of sulphite is possible, as in the case of some samples of American glucose, it is advisable to dilute the glucose (20 grams) or other substance with about one-fourth its bulk of water.* A slight excess of bromine water is then added, and the mixture heated until free from bromine; the solution is afterwards cooled, 8 c.c. of hydrochloric acid and 4 drops of cuprous chloride solution are introduced, and the whole is finally made up to 40 c.c. with water.

(1) 0·01 milligram of arsenious acid was treated with bromine water, the solution boiled until free from bromine, and the usual procedure followed.

(2) 0·01 milligram of arsenious acid was treated as usual, without the addition of bromine. The mercuric chloride paper in each case had practically the same tint, proving that a preliminary treatment with bromine has no effect on the result. Similar experiments

* The oxidation of sulphites by bromine, and subsequent reduction of the arsenic to the arsenious state by cuprous chloride, was first suggested by Allen (*Analyst*, 1901, **26**, 11).

were made with 0·04 milligram of arsenious acid, with the same result.

If phosphites or hypophosphites are present, the sample should be treated with bromine before examination.

In the quantitative determination of traces of arsenic by this method the following points should be observed.

(1) The amount of hydrochloric acid used, the final bulk of the liquid, and the size of the zinc rod should always be the same. The temperature should not vary to any marked extent.

(2) The reaction should always occupy the same time.

(3) When comparing the sample with known amounts of arsenious acid, the standard test must contain the same weight of the same substance as the sample, but free from arsenic.

(4) The same apparatus, or a duplicate, should always be used.

If a yellow stain is found on the mercuric chloride cap after the sample has been treated with bromine as described above, and the gas washed three times with cuprous chloride solution, then arsenic is present, because under these conditions no other element gives this reaction. Antimony, up to about 2500 times the weight of arsenic present, does not obscure the result, except in cases where large amounts of organic matter are present, when the proportion of antimony to arsenic is reduced.

The arsenious acid used in the experiments described in this paper was in the form of a dilute solution of sodium arsenite.

The cuprous chloride solution is prepared as follows. Sixteen grams of pure cupric oxide are dissolved in 110 c.c. of hydrochloric acid, 13 grams of thin copper foil are cut into small pieces, and boiled with the above solution for 25 minutes, the resulting solution of cuprous chloride is poured into 1000 c.c. of distilled water, and the white precipitate washed by decantation. The chloride is then dissolved in hydrochloric acid free from arsenic, 5 c.c. of this solution are evaporated to dryness and the residue weighed, the solution is then diluted with hydrochloric acid until 100 c.c. contains about 15 grams of cuprous chloride.

LXXXI.—*Vapour Pressure of Aqueous Ammonia Solution. Part I.*

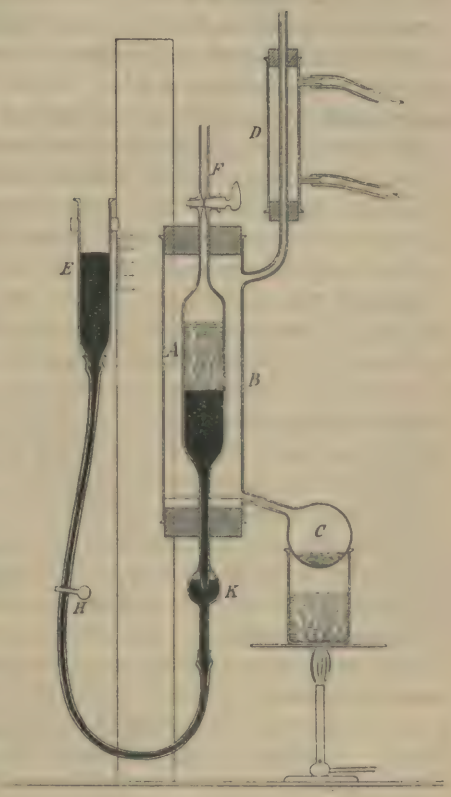
By Edgar Philip Perman, D.Sc.

The experiments described in this paper were undertaken at the direct instigation of Prof. Dewar, although the subject had naturally occurred to the author during his work on the rate of escape of ammonia from aqueous solution (Trans., 1898, 73, 511). The ob-

ject of the work was to discover the mode of variation of vapour-pressure of aqueous ammonia solution with variation in temperature and concentration, vapour pressure being measured by a statical method; and also to find the relation between vapour-pressure and "rate of escape."

Apparatus Employed.—The ammonia solution was introduced into the glass vessel, *A* (Fig. 1), shaped like a pipette; it was heated by a vapour-jacket in the surrounding vessel, *B*, the liquid producing the vapour being boiled in the bulb, *C*, and returning again to the liquid state in the condenser, *D*. The lower end of the vessel, *A*, was connected with a wide tube, *E*, by means of thick-walled rubber tubing; the tube, *E*, could be raised or lowered at will. The upper end of the vessel, *A*, was provided with a stopcock, *F*, immediately outside the split cork at the top of the jacketing vessel, *B*. A millimetre mirror scale stood behind, so that the level of the mercury in either tube could easily be read to 0·2 mm.

Fig. 1.



Method of Procedure.—Some strong ammonia solution (between 50 c.c. and 100 c.c.) was introduced into *A* through the stopcock, *F*. The rubber tube was clipped at *H*, and the tube above *F* connected with a water-air pump. The solution boiled violently, and after a short time the air in the upper part of the vessel and in the solution was expelled. The stopcock was then closed.

A determination of the strength of the ammonia solution left in the vessel *A* was then made by raising the tube, *E*, or pouring in mercury, and driving out some of the ammonia solution into a weighed quantity of dilute standard sulphuric acid until the acid was neutralised. The flask containing the acid and ammonia was

then weighed again, the contents were washed out, and the slight excess of ammonia titrated with standard sulphuric acid. The percentage of ammonia in the solution was then calculated from the data obtained. The results of different determinations for the same solution agreed very closely. The ammonia solution was then heated by the vapour-jacket to a known temperature, and the corresponding pressure read when it had become constant. Several readings were obtained by slightly raising or lowering the tube *E*; they varied usually not more than from 1 to 2 millimetres. The ammonia solution was then driven up to the stopcock; very often a minute bubble (presumably of air) remained undissolved; it was driven through the stopcock and fresh readings taken. There was an air-trap at *K*, but nevertheless traces of air were sometimes carried up.

In order to test the accuracy of the method, the vapour-pressure of water was determined at a temperature of 46·3° (vapour-jacket of carbon disulphide); the result obtained was 77·0 mm., while that calculated from Regnault's tables is 76·8 mm. at that temperature.

After a satisfactory set of readings had been made, the concentration of the ammonia solution was reduced by running a little water into the vessel *A*, and boiling off the air as before. A fresh set of readings for the new concentration was then made. More water was then run in, and so on. Corrections were made for the varying temperature of different parts of the mercury column. The density of the ammonia solution was taken from the ordinary density-concentration tables, no correction being made for temperature; the error caused by this is extremely small (*loc. cit.*, p. 524).

Preparation of Pure Ammonia Solution.—Pure ammonia was prepared by two methods given by Stas: (1) by heating ammonium sulphate with strong sulphuric acid and adding small quantities of nitric acid; (2) by heating ammonium chloride with strong nitric acid. In each case the ammonium salt remaining was decomposed by heating with a strong soda solution; the ammonia given off was freed from carbon dioxide by passing through milk of lime, and then led into water. The amount of amines in the ordinary ammonium salts is, however, very small. An experiment was made in order to determine the amount of carbon (in the form of amines) in concentrated ammonia solution such as is usually employed for analytical work.

A current of air freed from carbon dioxide was aspirated through 20 c.c. of the concentrated ammonia solution; the mixed gases were then led through an ordinary combustion tube containing copper oxide, and at the end a long roll of copper gauze. After leaving the combustion tube, the gases passed through a large calcium chloride tube, and finally through potash bulbs with a guard tube. From 20 c.c. of ammonia solution containing about 5·9 grams of ammonia, 0·02 gram

of carbon dioxide was obtained. On evaporating down, the ammonia solution was found to contain a trace of chloride.

Some of the experiments recorded were made with this solution, and the results cannot be distinguished from those given by the specially prepared ammonia solution.

Series of experiments were made at 0°, 20°, 34·4°, 46·4°, and 61·3°, the temperatures being obtained by means of melting ice, water from a large barrel, boiling ether, boiling carbon disulphide, and boiling chloroform respectively. The first two were maintained constant, but the others varied slightly with the variation of barometric pressure. In order to correct the readings obtained for these slight differences of temperature, a curve was drawn for each temperature, showing the variation of pressure with concentration. The variations of temperature were so small that a smooth curve could easily be drawn through (or nearly through) the experimental points.

Experimental Results.

Temperature 0°.

Series.	Pressure.	Per cent. of NH_3.	Series.	Pressure.	Per cent. of NH_3.
I.	61 mm.	16·11	III.	238·5 mm.	31·50
	41	12·11		178·5	27·44
	26·5	8·02		94·0	20·41
	20	4·21		42·5	11·88
II	275	32·68		31·5	8·74
	79·5	17·63	IV.	252·8	31·60
	36	8·08		116·2	23·21
	19	6·68		63·7	15·78
	17·5	4·89		41·6	11·56
				25·7	7·64
				22·8	5·99
				11·5	2·59

Temperature 20°.

Series.	Pressure.	Per cent. of NH_3.	Series.	Pressure.	Per cent. of NH_3.
	614·6 mm.	31·70	III.	86·2 mm.	8·16
	308·6	23·18		59·8	5·74
	208·3	18·43		51·3	4·80
	148·4	14·58			
II.	593·6	31·46			
	331·7	23·98			
	223·5	19·29			
	115·6	12·10			

Temperature 34·4°.

Series.	Pressure.	Per cent. of NH_3.	Temperature.	dp/dt.	Pressure at 34·4°.
I.	1352·3 mm.	34·74	34·0°	47·0	1369·1 mm.
	548·3	22·43	34·4	22·9	548·3
	346·3	17 06	33·8	15·5	355·6
	228·3	12·27	34·1	10·1	231·3
	155·8	8·26	34·1	6·35	157·7
	111·8	5·50	34·3	4·1	112·2
	89·8	3·91	34·4	—	89·8
II.	584·3	23·07	34·8	23·6	574·9
	297·8	14·90	34·8	12·9	292·6
	188·8	9·66	34·4	—	188·8
	143·8	8·28	34·3	6·35	144·4
	107·3	4·99	34·7	3·7	106·2
III.	1113·3	31·86	34·8	40·5	1097·1
	798·8	26·94	35·1	30·4	807·9
	549·3	22·39	34·8	22·9	540·1

Temperature 46·4°.

Series.	Pressure.	Per cent. of NH_3.	Temperature.	dp/dt.	Pressure at 46·4°.
I.	921·9 mm.	23·35	46·3°	37·3	925·6 mm.
	568·0	16·85	46·3	23·4	570·3
	411·7	13·02	46·3	17·2	413·4
II.	1443·9	29·75	46·4	—	1443·9
	841·3	21·88	46·3	33·9	844·7
	477·9	14·74	46·3	19·7	479·9
III.	1801·6	32·71	46·6	?	1810 ?
	1271·1	27·75	46·4	—	1271·1
	789·1	21·13	46·2	32·0	795·5
	574·1	17·07	46·4	—	574·1
	476·6	14·73	46·4	—	476·6
	372·3	11·90	46·4	—	372·3
	294·4	9·44	46·4	—	294·4
	241·5	7·57	46·3	9·8	242·5
	203·0	6·03	46·3	8·0	203·8
	163·3	4·32	46·4	—	163·3
IV.	745·3	20·34	46·4	—	745·3
	570·2	16·85	46·4	—	570·2
	324·9	10·17	46·4	—	324·9

Temperature 61·3°.

Series.	Pressure.	Per cent. of NH_3.	Temperature.	dp/dt.	Pressure at 61·3°.
I.	1637·4 mm.	23·77	60·9°	68·5	1664·8 mm.
	1069·9	18·01	60 9	42·2	1086·8
	770·7	13·92	60·8	31·8	786·6
	543·7	9·57	61·1	22·1	548·1
	407·1	6·56	61·2	16·1	408·7
	330·8	4·75	61·3	12·7	330·8
II.	1716·5	24·30	61·7	74·0	1686·9
	1223·0	19·41	61·7	46·3	1204·5
	778·2	13·58	61·7	31·0	765·8
	512·7	8·74	61·6	20·5	506·6
	371·5	6·10	60·2	15·2	388·2

From the series of isothermal curves obtained, values of pressure and temperature at different concentrations were read off, and a fresh series of curves showing variation of pressure with temperature was constructed. Tangents were then drawn to these curves at the points at which the values of dp/dt were required, and a series of curves drawn showing the variation of dp/dt with concentration at the mean temperature of each set of observations. The original observations were then corrected to the mean temperature of each set. In most cases, the corrections are very small.

In order to show that tangents drawn by eye are sufficiently accurate for the purpose, a curve was drawn in a similar way, showing the path of a body falling freely under the action of gravity, and tangents were drawn at different points; these give the velocities of the body after definite intervals of time. The following numbers were obtained:

	Velocity (from tangent). Feet per second.	Calc. velocity. Feet per second.
After 2 seconds.....	65·4	64
„ 3 „	96·2	96
„ 4 „	126	128
„ 5 „	157	160

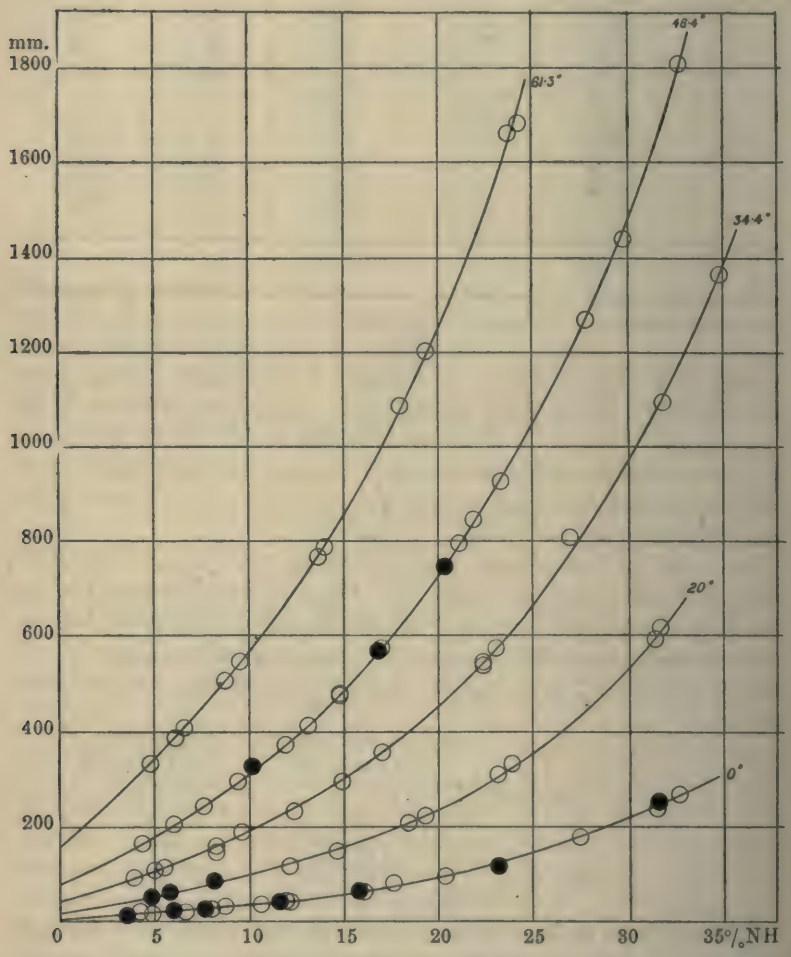
A fresh series of isothermal curves was then constructed from the corrected pressures; they are reproduced in Fig. 2 (p. 724).

Some results were also obtained at 0°, 20°, and 46·4° with a modified form of apparatus, the temperature being kept constant. The apparatus is described in the next paper; the points obtained with it are marked ● in Fig. 2, and are seen to confirm those given by the former method.

The table on p. 725 contains the pressures read from the smoothed curves.

Attempts have been made to find a simple relation between the vapour pressure and the concentration, and also between the vapour pressure and the temperature of the solution, but hitherto without

FIG. 2.



success in either case. The author is now investigating the partial pressures of the ammonia and of the water. No doubt the ammonia solution may be regarded as a mixture of two liquids of which the boiling points are far removed from one another. The determination of the partial pressures will make it possible to verify this supposition.

Isothermals.

Percentage of NH_3.	Pressure at 61·3°.	Pressure at 46·4°.	Pressure at 34·4°.	Pressure at 20°.	Pressure at 0°.
0	158 mm.	77 mm.	40 mm.	17 mm.	5 mm.
2·5	248	122	71	32	13
5·0	345	178	104	48	20
7·5	448	240	143	70	28
10·0	567	313	187	93	35
12·5	699	394	237	118	45
15·0	856	488	297	151	58
17·5	1035	597	369	190	75
20·0	1248	730	450	235	93
22·5	1500	879	549	291	117
25·0	? 1842	1050	672	360	145
27·5	—	1248	813	439	181
30·0	—	1478	970	535	220
32·5	—	1777	1154	656	264
35·0	—	—	1374	—	313

The author wishes, in conclusion, to express his thanks to the Research Fund Committee of the Chemical Society for their grant in aid of the expense incurred for apparatus, and he is indebted to Mr. G. A. S. Atkinson, of Cardiff, for assistance at various stages of the work.

University College,
Cardiff.

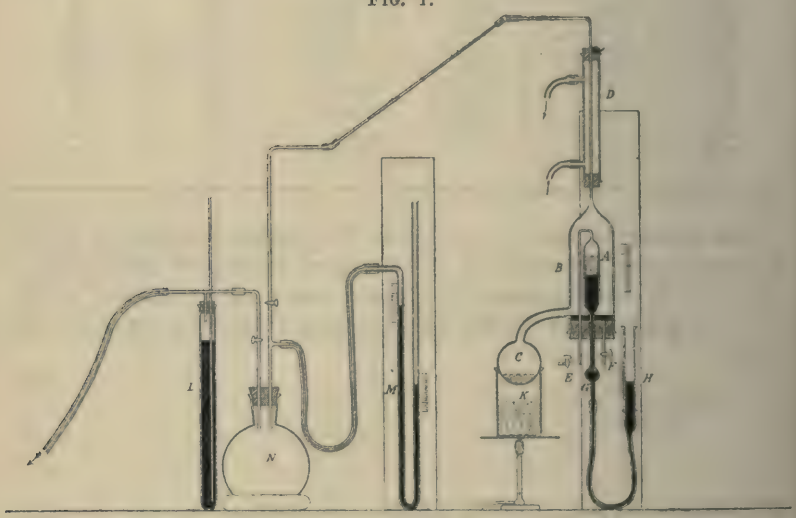
LXXXII.—*Influence of Sodium Sulphate on the Vapour Pressure of Aqueous Ammonia Solution.*

By Edgar Philip Perman, D.Sc.

This research was undertaken with the object of throwing further light, if possible, upon the question of the molecular condition of sodium sulphate in an aqueous solution. The author's investigations on the vapour pressure of aqueous ammonia solution have made this a comparatively easy task. A modified form of apparatus was used (Fig. 1, p. 726); it differs from that described in the previous paper in the following particulars. The solution was introduced into the vessel, *A*, by means of the capillary tube, *E*, which passes downwards through the rubber cork closing the outer vessel, *B*. The temperature was kept constant by means of the regulator, *L*, containing mercury. The globe, *N*, serves to steady the pressure. The water-air pump was made to draw air through the long centre tube of the regulator, and by altering the depth below the mercury of this tube, the pressure could be regu-

lated as desired; the pressure was read off on the gauge, *M*, connected with the large globe. Carbon disulphide was boiled in the bulb, *C*, and the pressures necessary to give the required temperatures were taken from the tables of Ramsay and Young. A solution was made up by dissolving pure crystalline sodium sulphate in aqueous ammonia solution; this was introduced into the vessel, *A*, as described, and remained there throughout each series of experiments. The tempera ture was varied from 26° to 47°, and a series of ten or twelve observations made with the same solution. The strength of the solution was

Fig. 1.



then found by drawing off two samples and estimating ammonia in one, by titration, and sodium sulphate in the other, by evaporation and ignition of the residue.

Experimental Results.

I.—Solution contained $NH_3 = 17{\cdot}47$ per cent. of the NH_3 and H_2O.
„ „ $Na_2SO_4 = 4{\cdot}23$ „ total solution.

Temp.	Press.	Temp.	Press.
27·6°	321·1 mm.	39·1°	497·3 mm.
31·1	364·0	40·3	523·3
33·0	395·1	42·0	550·4
35·2	433·1	43·0	580·9
37·0	467·0	44·7	619·3
37·0	476·7	46·5	666·5
38·5	485·2	35·2	438·3

II.—Solution contained $NH_3 = 16{\cdot}17$ per cent. of the NH_3 and H_2O.
„ „ $Na_2SO_4 = 4{\cdot}53$ „ total solution.

Temp.	Press.	Temp.	Press.
28·7°	238·8 mm.	39·4°	374·9 mm.
30·9	261·2	42·7	429·8
33·1	288·7	45·0	468·6
34·7	307·3	46·2	491·6
37·3	342·7	25·8	215·3

III.—Solution contained $NH_3 = 10{\cdot}34$ per cent. of the NH_3 and H_2O.
„ „ $Na_2SO_4 = 4{\cdot}25$ „ total solution.

Temp.	Press.	Temp.	Press.
29·3°	167·7 mm.	37·9°	246·0 mm.
31·1	183·5	40·1	271·6
33·4	202·8	43·1	310·4
34·8	215·9	46·2	352·8
36·5	232·4		

The results are shown in the curves in Fig. 2 (p. 728), the circles indicate (as their centres) the experimental points. The dotted lines I*a* and III*a* show the pressures for the corresponding solutions of ammonia, that is, having the same proportion of ammonia to water, but no sodium sulphate.

For curve II, the strength of the solution was not accurately determined owing to an accident. Curve I*b* shows the pressures that the ammonia solution would have, supposing the sodium sulphate present to hold its water of crystallisation in combination, $10H_2O$ for Na_2SO_4, and so increase the concentration of the ammonia solution. The solutions employed had the following percentage composition :

Solution.	NH_3.	Na_2SO_4.	H_2O.
I. ...	16·73	... 4·23	... 79·04
II. ...	(15 ?)	... 4·53	... —
III. ...	9·90	... 4·25	... 85·85

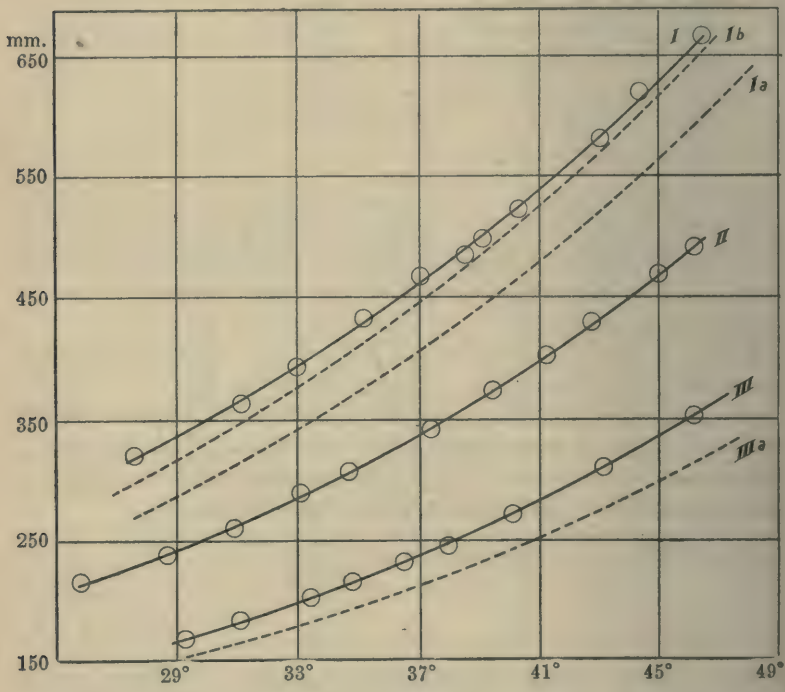
The ammonia solution was saturated with sodium sulphate in each case, and then a little water added to prevent the salt from crystallising out.

Discussion of Results.

It will be seen at once that the vapour-pressure of the ammonia solution is much increased by the presence of the sodium sulphate, and is actually higher than it would become supposing the hydrate $Na_2SO_4,10H_2O$ to be formed, and so increase the concentration of the ammonia solution. This effect is probably caused by a displacement, more physical than chemical, of the ammonia by the sodium sulphate.

An opposite effect would be produced by the partition of the acid between the soda and the ammonia, but the latter is such a weak base, compared with the former, that the result would be hardly appreciable. It is well known that the solubility curve of sodium sulphate shows a well-marked break at about 33°; below this temperature, the hydrated sulphate, $Na_2SO_4,10H_2O$, crystallises out, whilst above it the anhydrous salt separates on evaporation. It was thought that the vapour-pressure curve might show a similar break at the same temperature, but it will be seen at once that there is no trace of such a break, showing

FIG. 2.



that there cannot be any sudden change in the state of hydration of the salt. This appears to disprove at once the old theory that the solution contained hydrated molecules, $Na_2SO_4,10H_2O$, below 33°, and anhydrous molecules, Na_2SO_4, above that temperature. It favours, however, the modern explanation, namely, that the change is not in the solution but in the solid with which the solution is in contact, and that the solution contains only Na_2SO_4 molecules throughout.

Another possible explanation of the properties of the solutions observed is that they contain both anhydrous and hydrated molecules

the number of the former increasing, and of the latter diminishing, with rise of temperature; in that case, there should be a gradual divergence from one another of the curves for ammonia solution and for the same solution containing sodium sulphate. The curves in the diagram show a slight divergence, but apparently not more than there would be for ammonia solution itself of various concentrations. The experiments are probably not sufficiently accurate to decide this point, unless the dehydration of the molecules was completed within a very narrow range of temperature, and there is no sign of any such change.

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LXXXIII.—*The Synthetical Formation of Bridged Rings. Part I. Some Derivatives of Dicyclopentane.*

By W. H. PERKIN, jun., and J. F. THORPE.

A SHORT time ago (Trans., 1899, **75**, 48) we showed that ethyl bromodimethylglutarate, when digested with alcoholic potash, yields the potassium salt of *caronic acid*,

$$CO_2Et\cdot CHBr\cdot CMe_2\cdot CH_2\cdot CO_2Et + 4KOH = CO_2K\cdot CH\overset{CMe_2}{<}CH\cdot CO_2K + 2KBr + 2EtOH + 2H_2O,$$

and this synthesis not only proves the constitution assigned to caronic acid by Baeyer and Ipatieff (*Ber.*, 1892, **29**, 2796), but, indirectly, affords strong evidence that the formula of carone,

$$Me\cdot CH\overset{CH_2\cdot CH_2\cdot CH}{<}CO\overset{CH}{>}CMe_2,$$

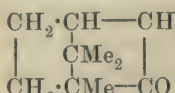
first suggested by Wagner (*J. Russ. Phys. Chem. Soc.*, 1896, **28**, 95) is correct. The saturated hydrocarbon,

$$CH_2\cdot CH_2\cdot CH\overset{CH_2\cdot CH_2\cdot CH}{<}CH_2,$$

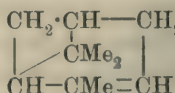
from which carone is derived, is therefore a heptamethylene ring in which two carbon atoms are united to form a trimethylene ring, or, in other words, it is made up of a hexamethylene and a trimethylene ring.

During the last few years, it has frequently been suggested that the constitutions of some members of the terpene and camphor series should be expressed by formulæ containing somewhat similar bridged

or double rings. Thus, for example, camphor and pinene should, according to Bredt, be represented thus:



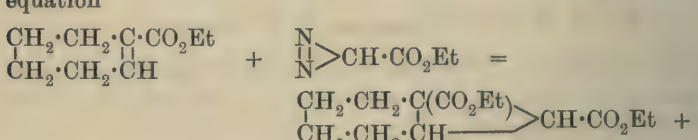
Camphor.



Pinene.

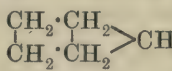
The camphor formula contains two five-carbon rings, the pinene formula, on the other hand, a six- and a four-carbon ring. As it is probable that compounds of this and other similar types will, in the near future, be of common occurrence, it seemed to us that it was a matter of importance to endeavour to discover synthetical methods for the formation of such double or *bridged* rings.

The only work which has been done in this direction is that of Buchner (*Ber.*, 1900, **33**, 3454), who has lately shown that ethyl tetrahydrobenzoate combines with ethyl diazoacetate according to the equation



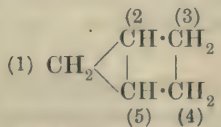
and the product, which he terms ethyl 1 : 2-norcarandicarboxylate, on account of its close relationship to carone, contains a *bridged* heptamethylene ring.

In the present paper, abstracts of which have already appeared (Proc., 1900, **16**, 149; 1901, **17**, 110), we describe the synthesis of a series of compounds derived from the hydrocarbon

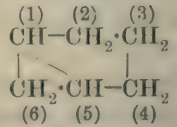


which consists of a pentamethylene ring so bridged as to form a four- and a three-carbon ring united together by two carbon atoms of each.

In endeavouring to devise a general system of nomenclature for bridged rings of this description, we met with very considerable difficulty. Our first suggestion was that the letters γεψ (from γεψυρα, a bridge) should be prefixed to the hydrocarbon, with numbers to indicate the carbon atoms which were united to form the bridge thus:—



2 : 5-γεψ-Pentamethylene



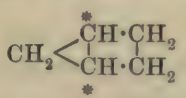
1 : 5-γεψ-Hexamethylene.

but this method cannot be well adapted to substances such as camphor and pinene (p. 730), in which the bridge itself consists of one or more carbon atoms.

In a letter to Professor von Baeyer, one of us mentioned this difficulty, and as the result of a good deal of correspondence, he was good enough to elaborate a scheme for the nomenclature of bridged rings which seems to be of general application, and was subsequently published (*Ber.*, 1901, **33**, 3771). Briefly stated, this scheme is as follows.

Every bridged (or dicyclic) hydrocarbon contains, of necessity, two tertiary carbon atoms which are either directly united to form the bridge, or else indirectly united when the bridge is itself made up of carbon atoms: in the first place, the bridge is called 0, in the second case 1, 2, &c., according to the number of carbon atoms which it contains.

Furthermore, every dicyclic hydrocarbon, contains three bridges as will be clearly seen from the study of the case of *di*cyclo*pentane*,



in which the bridges are, firstly, the direct union of the two tertiary carbon atoms (0), secondly, the bridge containing the CH_2 group (1), and thirdly, the bridge, $\cdot CH_2 \cdot CH_2 \cdot$ (2). This hydrocarbon, which is the only possible form of a bridged pentamethylene ring, would therefore be (0 : 1 : 2)-*di*cyclo*pentane*.

It is not possible in this paper to discuss this scheme in its entirety, but the case of the four *cyclo*heptanes given by von Baeyer (whose interesting paper should be consulted for further details) will illustrate its general applicability.



(0 : 1 : 4).



(0 : 2 : 3).

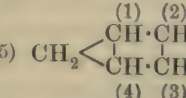


(1 : 2 : 2).



(1 : 1 : 3).

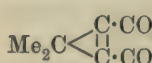
We propose to use this system in naming the derivatives of di*cyclo*pentane which we describe in this paper, and the positions occupied by the various substituting groups will be indicated by numbers according to the scheme.*



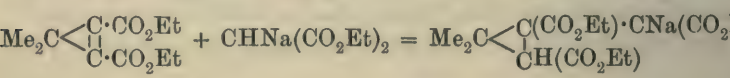
* Starting the numbering at one of the tertiary carbon atoms (compare Baeyer, *c. cit.*, p. 3774).

But for the sake of brevity in writing names, the numbers will always be omitted where the constitution of the substance referred to is sufficiently clear without numbering, and as there is only one possible di*cyclo*pentane the prefix (0 : 1 : 2) will also be neglected.

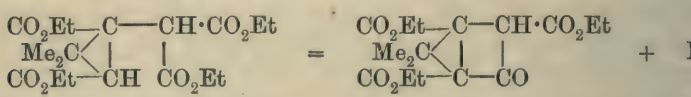
In commencing our experiments on the formation of di*cyclo*pentane derivatives, we endeavoured in the first place to prepare a dimethyltrimethenedicarboxylic ester of the formula



This ester contains a double bond between carbon atoms, both of which are combined with carbethoxy-groups, and might, therefore, be expected to react with the sodium compound of ethyl malonate to form the sodium compound of *ethyl dicarboxydimethyltrimethylenemalonate*,

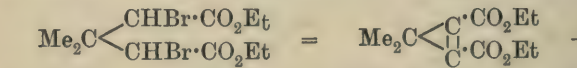


If, then, the ester obtained from this sodium compound by acidifying could be made to undergo condensation with elimination of alcohol, the process might take place thus:

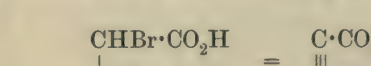


and the condensation product thus formed would be ethyl 5 : 5-dimethyl-3-ketodi*cyclo*pentane-1 : 2 : 4-tricarboxylate.

In order to obtain the dimethyltrimethenedicarboxylic ester necessary for these experiments, we prepared a quantity of *ethyl $\alpha\alpha_1$-dibromo-$\beta\beta$-dimethylglutarate* (p. 754), in the expectation that the elimination of 2 mols. of hydrogen bromide from this would proceed as follows:



a reaction very similar to the formation of acetylenedicarboxylic acid by the removal of 2 mols. of hydrogen bromide from dibromosuccinic acid.



This reaction seemed the more probable from the consideration of the fact that ethyl monobromodimethylglutarate, under suitable conditions, readily loses hydrogen bromide with formation of ethyl caronate (p. 729). In testing the matter experimentally, we found, however, that even by using the most varied conditions we were unable to isolate a trace of this unsaturated ester or the corresponding acid.

When ethyl dibromodimethylglutarate is digested with alcoholic potash or sodium ethoxide, the unsaturated ring is evidently formed in the first instance, but this is so reactive that it at once combines with the alcohol present to form *ethoxycaronic acid* (p. 759).



In a similar way, if methyl alcoholic potash is employed, the corresponding *methoxycaronic acid* (p. 761) is formed.

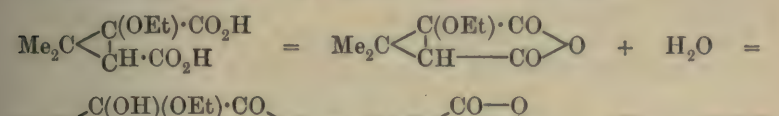
If the dibromo-ester is treated with aqueous potash, part of it is converted into the lactone of dihydroxydimethylglutaric acid (p. 756).

$$CO_2H{\cdot}CH(OH){\cdot}CMe_2{\cdot}CH(OH){\cdot}CO_2H\ ,*$$

and there is also formed some ethoxycaronic acid—an interesting result which shows that the unsaturated ring is so reactive that it even adds on the small quantity of alcohol which is produced by the hydrolysis of the ester, and this in the presence of large quantities of water. Experiments with diethylaniline, silver oxide, and other similar reagents in the place of potash were also made, but in no case could the desired unsaturated substance be isolated.

We were also unsuccessful in our attempts to remove alcohol from ethoxycaronic acid by means of sulphuric acid or other reagents having a strong affinity for alcohol.

When ethoxycaronic acid, for example, is warmed with 80 per cent. sulphuric acid, a remarkable decomposition takes place, carbon monoxide is evolved, and the solution, after adding water, is found to contain *aa*-dimethylsuccinic acid (p. 762). This process, which seems to proceed quantitatively, is probably represented thus:

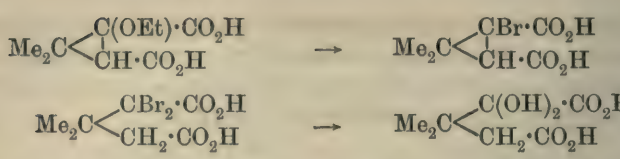


Still more interesting is the behaviour of ethoxycaronic acid on treatment with hydrobromic acid, when it is converted, with disruption of the trimethylene ring, into a bromo-acid, which is evidently *aa-dibromodimethylglutaric acid*, since on boiling with water it is converted into *aa-dihydroxydimethylglutaric acid*. This process may be formulated thus:

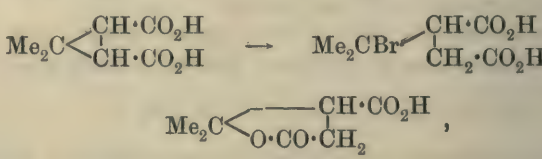
* A very small quantity of *aa*-dihydroxydimethylglutaric acid,

$$CO_2H{\cdot}C(OH)_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H,$$

was also produced in this experiment, which proves that the bromo-ester must have contained traces of ethyl *aa*-dibromodimethylglutarate (see p. 757).



This change is very similar to the conversion of caronic acid into terebic acid by the action of hydrobromic acid (Baeyer and Ipatieff, *Ber.*, 1896, **29**, 2801).

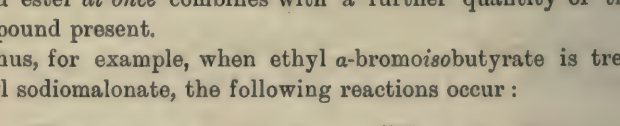


the addition of hydrogen bromide taking place, however, in the two cases in different directions, which is rather curious.

Since we were unable to isolate the unsaturated ester which we required for the synthesis of derivatives of di*cyclo*pentane, we next attempted to use this unsaturated ester in a nascent state, and ultimately we were successful in our endeavours.

In investigations on the behaviour of bromo-esters on treatment with ethyl sodiomalonate and other analogous sodium compounds, it has frequently been noticed that the constitution of the product formed shows that the reaction must have proceeded in two stages. (1) The alkaline sodium compound causes elimination of hydrogen bromide and formation of an unsaturated ester, and (2) the unsaturated ester *at once* combines with a further quantity of the sodium compound present.

Thus, for example, when ethyl *a*-bromo*iso*butyrate is treated with ethyl sodiomalonate, the following reactions occur:



It therefore seemed possible that, under similar circumstances, ethyl dibromodimethylglutarate might first be converted into the unsaturated compound, and that this might then *at once* combine with excess of ethyl sodiomalonate, this addition taking place more rapidly than the addition of alcohol to form ethoxycaronic ester.

The intermediate formation of the unsaturated ester, in this reaction, seemed all the more likely from the fact that when ethyl

dibromodimethylglutarate is treated with sodium ethoxide in alcoholic solution *ethyl ethoxycaronate* is formed.

$$Me_2C\begin{<}CHBr\cdot CO_2Et\\CHBr\cdot CO_2Et\end{>} \rightarrow Me_2C\begin{<}C\cdot CO_2Et\\\|\\C\cdot CO_2Et\end{>} \rightarrow Me_2C\begin{<}C(OEt)\cdot CO_2Et\\|\\CH\cdot CO_2Et\end{>},$$

and not ethyl diethoxydimethylglutarate.

$$CO_2Et\cdot CH(OEt)\cdot CMe_2\cdot CH(OEt)\cdot CO_2Et.$$

On testing this hypothesis experimentally, it was found that a yield of 50—60 per cent. of an ester, which boiled at 234° under 20 mm. pressure, was obtained in this way, and analysis showed that this ester had the composition of the condensation product,

$$Me_2C\begin{<}C(CO_2Et)\cdot CH(CO_2Et)_2\\CH\cdot CO_2Et\end{>} \quad \text{I.}$$

which we were endeavouring to prepare (p. 762).

Before using this ester for synthetical work, however, it was most necessary to carefully prove its constitution, since the reaction between the ethyl sodiomalonate and the dibromo-ester might take place in a different way with formation of a derivative of tetramethylene, exactly as is the case when trimethylene bromide reacts with ethyl sodiomalonate.

$$CH_2\begin{<}CH_2Br\\CH_2Br\end{>} + Na_2C(CO_2Et)_2 = CH_2\begin{<}CH_2\\CH_2\end{>}C(CO_2Et)_2 + 2NaBr$$

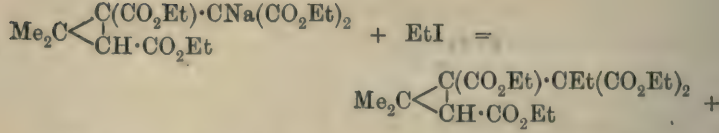
$$Me_2C\begin{<}CHBr\cdot CO_2Et\\CHBr\cdot CO_2Et\end{>} + Na_2C(CO_2Et)_2 =$$

$$Me_2C\begin{<}CH\cdot CO_2Et\\>C(CO_2Et)_2\\CH\cdot CO_2Et\end{<} + 2NaBr$$

Ethyl dimethyltetramethylene-tetracarboxylate. II.

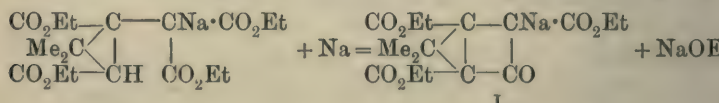
It was not easy to decide between the trimethylene formula, I, and the tetramethylene formula, II, for this ester, but ultimately it was shown in the following way that this substance must be the trimethylene derivative.

If the two possible formulæ are examined, it will be seen that the trimethylene derivative still contains the group $\cdot\overset{*}{C}H(CO_2Et)_2$, and must therefore be capable of forming a sodium compound which should react with alkyl haloids, whereas the tetramethylene derivative contains no such hydrogen atom capable of being replaced by sodium. We therefore treated the ester with sodium ethoxide and ethyl iodide, and obtained at once and in almost quantitative yield the corresponding ethyl derivative.



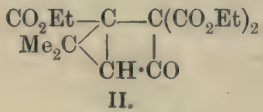
The formation of this ester, a description of the properties of which is given on p. 770, proves conclusively that the product of the action of ethyl dibromodimethylglutarate on the sodium compound of ethyl malonate is *ethyl dicarboxydimethyltrimethylenemalonate* of the constitution represented by formula I.

When this ester, dissolved in boiling xylene, is treated with sodium, or when its alcoholic solution is boiled with sodium ethoxide, a very remarkable reaction takes place, alcohol is eliminated as sodium ethoxide, and a bright yellow, very stable sodium compound is produced. Our experiments seem to us to prove conclusively that the formation of this sodium compound must be expressed in the following way:

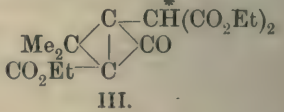


I.

There are two other possible ways in which the ester could undergo internal condensation with elimination of alcohol, that is to say, substances of the following constitutions might conceivably be produced:



II.



III.

The ester (II) contains no hydrogen atom replaceable by sodium and could not therefore yield the yellow sodium compound, which is actually formed in the reaction, and although in formula III the hydrogen atom, H*, would be replaceable by sodium, an extended examination of the substances obtained in various ways from the yellow sodium compound clearly proves that this expression cannot be correct, and that the true constitution of the yellow sodium compound is that represented by formula I and it is therefore the sodium compound of ethyl 5 : 5-dimethyl-3-ketodi*cyclo*pentane-1 : 2 : 4-tricarboxylate.[1]

During the course of this investigation, we discovered that this same yellow sodium compound is directly produced when ethyl dibromodimethylglutarate (1 mol.) is digested in alcoholic solution with 2 mols. of ethyl malonate and 4 mols. of sodium ethoxide (p. 776) and as the yield obtained in this way is 70 per cent. of the theoretical, and the

[1] Dieckmann (*Ber.*, 1900, **33**, 2678) has also expressed the opinion that the formula which we have assigned to this sodium compound is correct.

method is by far the most convenient, it was used in preparing almost the whole of the yellow sodium compound necessary for this research.

In considering the formation of this sodium compound, it should be noted that it is most unusual for alcohol to be eliminated in reactions of this kind in the way represented above, and this is at once evident from a brief consideration of Claisen's work on this subject. In such condensations, as for example, in the formation of ethyl acetoacetate from ethyl acetate, Claisen has shown that the first stage is the addition of sodium ethoxide to the carbethoxy-group of one of the reacting molecules, and that the sodium compound, thus produced, then condenses with the second molecule.

$$(1)\quad CH_3\cdot C\overset{O}{\underset{OEt}{<}} + NaOEt = CH_3\cdot C\begin{cases}ONa\\Et\\OEt\end{cases}$$

$$(2)\quad CH_3\cdot C\begin{cases}ONa\\OEt\\OEt\end{cases} + CH_3\cdot CO_2Et = CH_3\cdot C(ONa){:}CH\cdot CO_2Et + 2EtOH.$$

Condensations of this nature have, so far, only been known to take place when the conditions necessary for the elimination of 2 molecular proportions of alcohol were present. Thus ethyl acetate condenses with ethyl butyrate, $CH_3\cdot CH_2\cdot \overset{*}{C}H_2\cdot CO_2Et$, but not with ethyl *iso*butyrate, $(CH_3)_2CH\cdot CO_2Et$, because the former does, but the latter does not, contain the two α-hydrogen atoms necessary for the formation of 2 mols. of alcohol according to equation 2.

It is, however, quite conceivable that such condensations may, under favourable circumstances, take place with elimination of only 1 mol. of alcohol according to the scheme,

$$R\cdot C(ONa)(OEt)_2 + R_2CH\cdot CO_2Et - EtOH = R\cdot C(ONa)(OEt)\cdot CR_2\cdot CO_2Et = R\cdot CO\cdot CR_2\cdot CO_2Et + NaOEt,$$

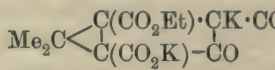
and we believe that the formation of the yellow sodium compound is a case of this kind.

The yellow sodium compound is very sparingly soluble in water, and is only very slowly acted on even by boiling water; it crystallises from alcohol in bright, orange-yellow, glistening plates and in appearance and several of its properties closely resembles the orange-yellow, crystalline, sodium compound of ethyl dicarboxyglutaconate,

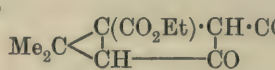
$$(CO_2Et)_2CNa\cdot CH{:}C(CO_2Et)_2,$$

which Conrad and Guthzeit (*Annalen*, 1883, 222, 250) first prepared by the action of chloroform on ethyl sodiomalonate. Like this substance, the solution of the yellow sodium compound in alcohol gives with ferric chloride an intense reddish-violet coloration.

When the yellow sodium compound is decomposed by acids, a colourless oil is obtained which doubtless consists of *ethyl dimethylketodi*cyclo*pentanetricarboxylate* and if this ester or the sodium compound is left in contact with methyl alcoholic potash, a curious decomposition takes place with formation of the *potassium* compound of *potassium diethyl dimethylketodi*cyclo*pentanetricarboxylate*,

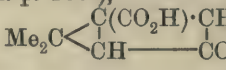


This on acidifying gives the free diethyl hydrogen salt which crystallises in colourless needles melting at 75° and on distillation, loses carbon dioxide with formation of *ethyl dimethylketodi*cyclo*pentanedicarboxylate*,

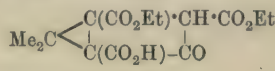


a colourless oil distilling at 201° under 30 mm. pressure and giving in alcoholic solution an intense reddish-purple coloration with ferric chloride.*

The free acid, which is readily obtained from this ester by hydrolysis with alcoholic potash, is readily soluble in water, melts at 180°, and when its aqueous solution is heated at 180° is decomposed with loss of carbon dioxide and formation of *dimethylketodi*cyclo*pentanecarboxylic acid* (m. p. 180°),

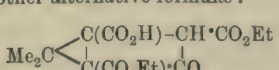


* The behaviour of this ester with ferric chloride, taken in connection with the constitution of the yellow sodium compound, clearly indicates the course of the reaction which takes place in the formation of the dipotassium diethyl salt, and seems to us to prove that the diethyl hydrogen salt (m. p. 75°) obtained by acidifying the dipotassium salt must have the constitution

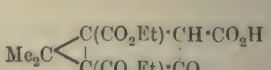


I.

The other alternative formulæ:



II.



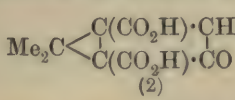
III.

are, in our opinion, not possible, for the following reasons.

In formula II, the carboxyl group is not attached to a carbon atom united to the CO group, and therefore it is unlikely that it would be so readily eliminated as is actually the case; a compound having formula III would, on distillation, yield a diethyl ester which would not be capable of giving a coloration with ferric chloride. Furthermore, it will be seen from the following pages that formula I explains in a satisfactory manner the formation and properties of the numerous substances we have prepared from the diethyl hydrogen salt.

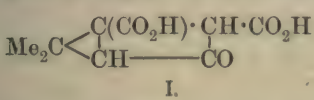
which is sparingly soluble in water and gives no coloration with ferric chloride.

When the yellow sodium compound, instead of being left in contact with methyl alcoholic potash, is boiled with alcoholic potash, it is converted into a mixture of two isomeric dibasic acids, $C_9H_{10}O_5$, melting at 155° and 180°, and called respectively A and B, the latter being identical with the acid of the same melting point mentioned above. Obviously during the hydrolysis the sodium compound is first converted into *dimethylketodicyclopentanetricarboxylic acid*,

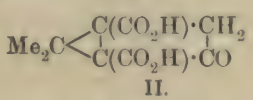


which then loses carbon dioxide with formation of the two isomeric dibasic acids.

If the formula of the tribasic acid is examined, it will be seen that two of the carbon atoms, marked (1) and (2), should be readily eliminated on hydrolysis with potash, since both are attached to carbon atoms joined to a CO group (as in the case of acetoacetic acid, acetonedicarboxylic acid, &c.). If, then, we suppose that different carboxyl groups have been removed in the formation of the isomeric dibasic acids, these would have the following formulæ :

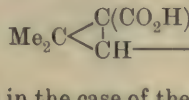


I.



II.

and the one having the constitution represented by the first formula would give a coloration with ferric chloride, whereas the other would not. Experiment, however, shows that both the acids give colorations with ferric chloride, that produced in the case of the acid melting at 155° being an intense bluish-violet, whereas the aqueous solution of the acid melting at 180° gives a reddish-violet. Both these acids, when heated, lose 1 mol. of carbon dioxide, and are converted into *dimethylketodicyclopentanecarboxylic acid*,

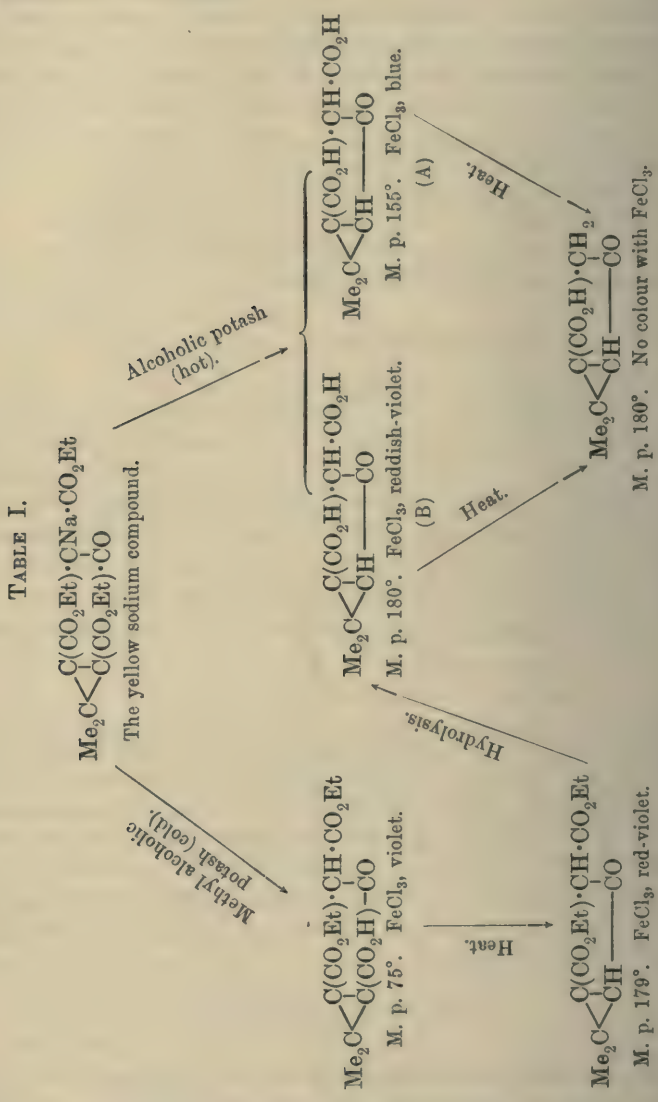


the change taking place in the case of the acid melting at 155° on simply boiling with dilute sulphuric acid, whereas, in the case of the acid melting at 180°, it is necessary to heat with water at 180°. The general behaviour of the two dibasic acids leads us to believe that they are not structurally different, but simply stereoisomeric modifications of the formula I given above.

In order that the relationships between these various substances

may be clearly seen at a glance, we give the following table, showing their methods of formation:

TABLE I.



Oxidation of Dimethylketodicyclopentanecarboxylic Acid,

$$Me_2C\begin{cases}C(CO_2H)\cdot CH_2\\ CH\text{——}CO\end{cases}.$$

In order to obtain as much evidence as possible in favour of the constitution we have assigned to this acid, we next studied its behaviour

on oxidation with nitric acid under various conditions, when it was found to yield, besides *aa-dimethylsuccinic acid*, $CO_2H{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$, a new dibasic acid of the formula $C_7H_{10}O_5$ and melting at 84°. For a considerable time, we were unable to discover the nature of this acid, which is the principal product of the oxidation; but ultimately we succeeded in proving conclusively that it has the constitution

$$CO_2H{\cdot}C(OH)_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H,$$

and is therefore *aa-dihydroxy-ββ-dimethylglutaric acid*.

In the first place, we showed that the new acid was not the *aa*$_1$-*dihydroxydimethylglutaric acid*, $CO_2H{\cdot}CH(OH){\cdot}CMe_2{\cdot}CH(OH){\cdot}CO_2H$, by preparing this acid, or rather its lactone,

$$Me_2C\begin{<}\begin{matrix}CH(OH)\text{—}CO\\ CH(CO_2H){\cdot}O\end{matrix},$$

from *aa*$_1$-dibromodimethylglutaric acid by a series of reactions described later (pp. 755, 756).

This lactone melts at 142°, and is quite different in its other properties from the acid melting at 84°. We next found that the new acid of melting point 84°, although it has the formula $C_5H_{10}O_2(CO_2H)_2$, and forms a *calcium* salt, $C_5H_{10}O_2(CO_2)_2Ca$, behaves in many of its reactions as a ketonic acid, $C_4H_8{\cdot}CO(CO_2H)_2$, containing 1 mol. of water less; thus it combines with phenylhydrazine and gives, with *o*-tolylenediamine, a well characterised condensation product derived from an acid of the latter formula.

In its properties, this acid shows considerable similarity to glyoxylic acid which crystallises in prisms having the formula $CH(OH)_2{\cdot}CO_2H$, and forms salts of the general formula $CH(OH)_2{\cdot}CO_2M$. On the other hand, glyoxylic acid shows the properties of the aldehydo-acid, $CHO{\cdot}CO_2H$, containing 1 mol. of water less, since it combines with hydroxylamine to form oximidoacetic acid, $OH{\cdot}N{:}CH{\cdot}CO_2H$, and on treatment with phenylhydrazine is converted into phenylhydrazineglyoxylic acid, $C_6H_5{\cdot}N_2H{:}CH{\cdot}CO_2H$. This striking similarity in properties leads us to the conclusion that in the crystalline state and in its salts this new acid (m. p. 84°) is *aa-dihydroxydimethylglutaric acid*, of the formula

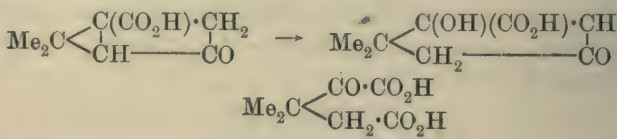
$$CO_2H{\cdot}C(OH)_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H,$$

but that, under suitable conditions, it can react as the corresponding ketonic acid, $CO_2H{\cdot}CO{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$. Since glyoxylic acid, on reduction, yields glycollic acid, we investigated the action of reducing agents on our new acid, and found that this behaved in an exactly analogous manner, yielding the *lactone* of *α-hydroxydimethylglutaric acid* (m. p. 112°, p. 758).

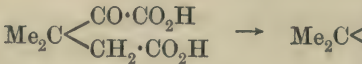
$$\begin{matrix}CH(CO_2H){\cdot}CMe_2{\cdot}CH_2\\ O\text{——————}CO\end{matrix},$$

a substance which we had previously obtained (Trans., 1899, 75, 56) by the action of sodium carbonate on ethyl hydrogen α-bromodimethylglutarate.

In order to explain the formation of αα-dihydroxydimethylglutaric acid from dimethylketodi*cyclo*pentanecarboxylic acid, it may be assumed that, at one stage of the oxidation, the trimethylene ring is split by the addition of water, and that the hydroxy-derivative formed is further oxidised to the ketonic acid, thus:



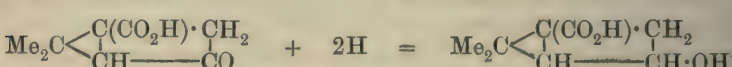
The dimethylsuccinic acid formed, in small quantity, at the same time is evidently produced by the further oxidation of the ketonic acid,



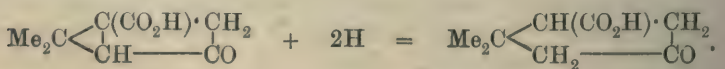
The formation of αα-dihydroxydimethylglutaric acid from ethoxycaronic acid by the action of hydrobromic acid (p. 762) and from αα-dibromodimethylglutaric acid by means of sodium carbonate subsequently plàced the constitution of this acid beyond question.

*Reduction of Dimethylketodi*cyclo*pentanecarboxylic Acid.*

When this acid is treated with sodium amalgam (p. 782), it readily takes up two hydrogen atoms, with formation of an acid of the formula $C_8H_{12}O_3$ (m. p. 103°), which at first was thought to be the corresponding hydroxy-acid.

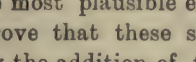


Since, however, the reduced acid yields a well characterised *semicarbazone*, it obviously still contains a ketonic group, and this fact, taken in connection with the other properties of the acid, shows that the two atoms of hydrogen which have been taken up have severed the trimethylene ring, this curious change occurring before the reduction of the ketonic group.

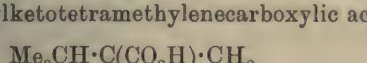


The acid $C_8H_{12}O_3$, which is therefore *dimethylketopentamethylenecarboxylic acid*, is not easily acted on by sodium amalgam, but if a

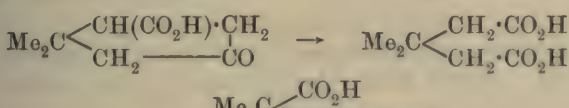
large excess is employed, it is ultimately reduced to the corresponding *hydroxydimethylpentamethylenecarboxylic acid* (m. p. 115°).



Although this is the most plausible expanation of these facts, it was still necessary to prove that these substances were pentamethylene derivatives, since by the addition of two atoms of hydrogen the trimethylene ring might be broken in two other directions, yielding two *iso*propylketotetramethylenecarboxylic acids of the formulæ:



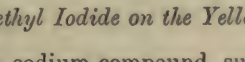
It was fortunately found to be a comparatively easy matter to prove that the constitution assigned to dimethylketodi*cyclo*pentanecarboxylic acid is correct, since experiment showed that this acid, on oxidation with nitric acid, yields *ββ*-dimethylglutaric acid and *αα*-dimethylsuccinic acid thus:



This process is exactly similar to that which has repeatedly been observed in the case of the oxidation of *cyclo*ketonic compounds; thus nitric acid oxidises ketopentamethylene to glutaric acid (Wislicenus and Hentzschel, *Annalen*, 1893, 275, 321), and ketohexamethylene to adipic acid (Wislicenus and Mager, *ibid.*, 363), and the formation of dimethylglutaric acid in the above oxidation clearly shows that dimethylketodi*cyclo*pentanecarboxylic acid cannot be a derivative of *iso*propylketotetramethylene.

Action of Methyl Iodide on the Yellow Sodium Compound.

When the yellow sodium compound, suspended in methyl alcohol, is boiled with methyl iodide, decomposition readily takes place with elimination of sodium iodide and formation of *ethyl* 5 : 5 : 2-*trimethylketodi*cyclo*pentanetricarboxylate* (p. 786).

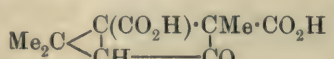


a colourless oil which distils constantly at 219° under 20 mm. pressure.

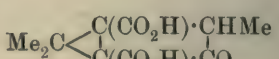
This ester on hydrolysis with methyl alcoholic potash in the cold is converted into the corresponding colourless, crystalline potassium salt

of the formula $C_8H_9O(CO_2K)_3$, and this when acidified is decomposed with elimination of carbon dioxide and formation of a crystalline acid melting at 146°.

Since this acid is dibasic, its constitution may be represented by either of the formulæ



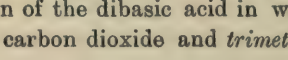
I.



II.

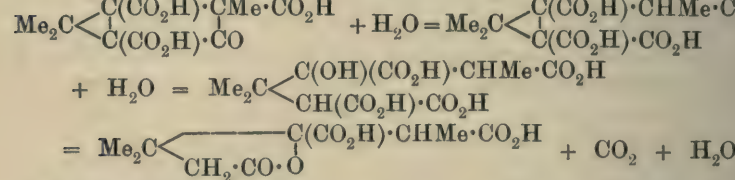
and although we consider I the more probable, the evidence at our disposal is not sufficient to enable us to definitely decide between the two possibilities.

When the solution of the dibasic acid in water is heated at 180°, it is decomposed into carbon dioxide and *trimethylketodicyclopentanecarboxylic acid*,



a crystalline acid which melts at 134°, is sparingly soluble in water and, as a ketonic acid, readily yields a semicarbazone.

Quite unexpected and very interesting results were obtained in investigating the action of boiling ethyl alcoholic potash on ethyl trimethylketodi*cyclo*pentanetricarboxylate. The product of this reaction, which is a substance sparingly soluble in water and melting at 237°, has been clearly proved to be the *lactone* of *hydroxytrimethylbutanetricarboxylic acid* (p. 788), and it must be assumed that in its formation 2 mols. of water have been taken up with consequent complete disruption of the di*cyclo*pentane ring, probably according to the scheme:



In formulating the process in this way, we have been guided by the following properties of the acid:

(1) It is a dibasic lactonic acid which yields a *silver* salt, $C_{10}H_{12}O_6Ag_2$, and when boiled with baryta it is hydrolysed with formation of the tribasic *barium* salt, $C_{20}H_{26}O_{14}Ba_3$.

(2) The difficulty with which it is hydrolysed on boiling with water indicates that it is most probably a γ-lactone.

(3) When treated with acetyl chloride, it is converted into an anhydride melting at 94—96°, and this on treatment with alkalis yields again the same acid melting at 237°. The ease with which this an-

hydride is formed points to the probability of the two carbon atoms being attached to neighbouring carbon atoms, as in succinic acid.

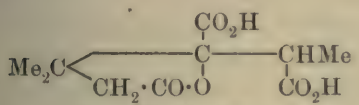
All these points are brought out in the formula represented above.

It is, however, obvious that disruption of the trimethylene ring may take place in other ways with formation, for example, of a substance of the formula

$$\begin{matrix} Me_2CH\cdot C(CO_2H)\cdot CHMe \\ CO_2H\cdot CH\text{—}O\text{—}CO \end{matrix}$$

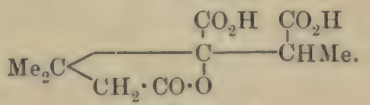
We hope to be able, at a later stage, to investigate the decomposition of this and other similar lactones described in this paper by fusion with potash (Baeyer, *Ber.*, 1896, **29**, 2795), in order to definitely prove their constitution.

When the lactonic acid melting at 237° is distilled under diminished pressure and the distillate boiled with water, an isomeric acid melting at 181° is obtained, which on treatment with acetyl chloride yields an anhydride melting at 131°. This anhydride on boiling with water is again converted into the acid melting at 181°. From this behaviour, it is obvious that this lactone of hydroxytrimethylbutanetricarboxylic acid exists in two isomeric forms, which may be represented thus:



trans-Modification.

Acid melts at 237°.
Anhydride melts at 96°.



cis-Modification.

Acid melts at 181°.
Anhydride melts at 131°.

These lactonic acids are very similar in constitution to the lactones of cis- and trans-*hydroxycamphoronic acid*, $\begin{matrix} Me_2C\text{—}CO\text{—}O \\ MeC(CO_2H)\cdot CH\cdot CO_2H \end{matrix}$ (Bredt, *Annalen*, 1898, **299**, 136), which also yield anhydrides. They have also many points in common with the lactone of *α-hydroxydimethyltricarballylic acid*, $\begin{matrix} Me_2C\cdot CH(CO_2H)\cdot CH\cdot CO_2H \\ CO\text{————}O \end{matrix}$ (Baeyer, *Ber.*, 1896, **29**, 2794).

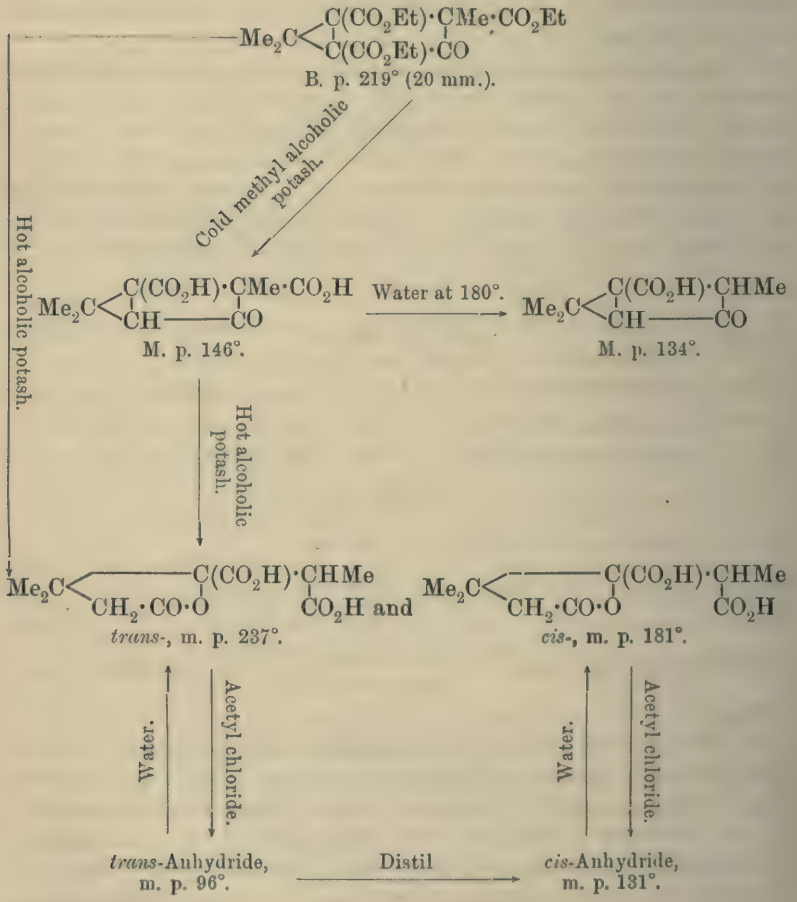
In searching the literature for examples of the disruption of the trimethylene ring by means of alkali, we have been able to find only one case, which, however, is of an almost identical nature with that described above. Buchner and Witter (*Ber.*, 1894, **27**, 871) found that methyl dicarboxytrimethyleneacetate, when hydrolysed with caustic soda, did not yield the corresponding acid, but was converted, with disruption of the trimethylene ring and loss of carbon dioxide, into a dibasic lactonic acid (Paraconcarbonessigsäure).

$CO_2Me\cdot CH_2\cdot C(CO_2H)<\begin{matrix}CH\cdot CO_2Me\\ CH\cdot CO_2Me\end{matrix}$ gives

$CO_2H\cdot CH_2\cdot CH<\begin{matrix}\text{———}CH\cdot CO_2H\\ CH_2\cdot CO\cdot O\end{matrix}$.

In order that our interpretation of the somewhat complicated decompositions, which are described above, may be clearly understood, we append a table of the various substances which have been obtained from the product of the action of methyl iodide on the yellow sodium compound:

TABLE II.



Examination of the Behaviour of Ethyl Dicarboxydimethyltrimethylene-malonate, $Me_2C<\begin{matrix}C(CO_2Et)\cdot CH(CO_2Et)_2\\ CH\cdot CO_2Et\end{matrix}$.

When this ester is digested with alcoholic potash, it yields two isomeric substances, $C_9H_{12}O_6$, which melt, or rather decompose, at 158° and 188° respectively, and both of which are *dibasic lactonic acids*. The behaviour of this ester with alcoholic potash is thus very similar to that just described in the case of ethyl trimethylketodi*cyclo*pentanetricarboxylate, the trimethylene ring suffering disruption under the influence of the alkali. The constitution of these two lactonic acids may very probably be expressed by the formulæ

$$Me_2C<\begin{matrix}\text{———}C(CO_2H)\cdot CH_2\cdot CO_2H\\ CH_2\cdot CO\cdot O\end{matrix}\qquad Me_2C<\begin{matrix}CH(CH_2\cdot CO_2H)\\ CH(CO_2H)\text{—}O\end{matrix}>CO,$$

I. II.

which represent them as structurally isomeric *lactones* of two *hydroxydimethylbutanetricarboxylic acids*. When these acids are heated, they decompose readily with evolution of carbon dioxide and formation of two different monobasic lactonic acids, $C_8H_{12}O_4$, which melt at 154° and 108° respectively.*

Arguing by analogy, it is most probable that the carboxyl group, which is eliminated from I in this process, is that which is attached to the tertiary carbon atom, especially as that atom is also united to the oxygen atom of the lactone ring. The *lactone* of *hydroxydimethylbutanedicarboxylic acid* obtained from I will then be

$$Me_2C<\begin{matrix}\text{———}CH\cdot CH_2\cdot CO_2H\\ CH_2\cdot CO\cdot O\end{matrix}\quad \text{III.}$$

With regard to formula II, there are two possible monobasic lactonic acids which may result from the elimination of carbon dioxide, namely,

$$Me_2C<\begin{matrix}CH(CH_2\cdot CO_2H)\\ CH_2\text{———}O\end{matrix}>CO\qquad Me_2C<\begin{matrix}CH(CH_3)\text{———}\\ CH(CO_2H)\cdot O\end{matrix}>CO,$$

IV. V.

but of these two possibilities, the lactonic acid represented by V has already been prepared by Balbiano (*Ber.*, 1894, **27**, 2136; 1895, **28**, 1508; compare Mahla and Tiemann, *Ber.*, 1895, **28**, 2161), it melts at 164°, and is, apparently, different from the acid obtained by us. We are, therefore, of opinion that the constitutions of the *lactones* of the two *hydroxybutanecarboxylic acids* melting at 158° and 188° are re-

* If the acid melting at 158° and 188° had been stereoisomeric as in the case of their methyl derivatives (p. 745), they would doubtless have been converted into the same acid by the action of heat and elimination of carbon dioxide.

presented by I and II, but we have not, as yet, sufficient evidence to enable us to decide which of these belongs to the substance of melting point 158° and which to that of melting point 188°; we propose, in the meantime, to name the first of these *A* and the second *B*. Similarly, we propose to name the monobasic lactonic acids melting at 154° and 108°, which are probably represented by III and IV, the lactones of *A*- and *B-hydroxydimethylbutanedicarboxylic acid*.

When ethyl dicarboxydimethyltrimethylenemalonate is treated with bromine, it is readily attacked with evolution of hydrogen bromide and formation of *ethyl dicarboxydimethyltrimethylenebromomalonate* (p. 769),

$$Me_2C\begin{<}C(CO_2Et)\cdot CBr(CO_2Et)_2\\CH\cdot CO_2Et\end{>},$$

and we have carefully studied the action of alcoholic potash on this compound, in the hope that hydrogen bromide might be eliminated in the apparently only possible direction, with formation of the acid,

$$Me_2C\begin{<}C{-}CO_2H\\ \\C{-}CO_2H\end{>}C(CO_2H)_2,$$

which is a derivative of *dicyclotetrane*.

We obtained in this way a monobasic anhydro-acid melting at 207°, which, on treatment with alkalis, is converted into a tribasic acid. Since this substance has the formula $C_9H_{10}O_5$, it is probably *anhydrodimethyltetramethylenetricarboxylic acid*,

$$Me_2C\begin{<}CH(CO_2H)\cdot CH\cdot CO\\ \\CH\cdot CO\end{>}O,$$

reduction of the di*cyclo*tetrane ring having taken place during hydrolysis. This reaction is being further investigated.

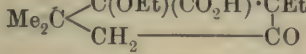
Investigation of Ethyl Dicarboxydimethyltrimethylene-ethylmalonate,

$$Me_2C\begin{<}C(CO_2Et)\cdot CEt(CO_2Et)_2\\CH\cdot CO_2Et\end{>}.$$

The principal product of the action of alcoholic potash on this ester is a crystalline substance, $C_{13}H_{20}O_6$, which melts at 175°, and the silver salt of which has the formula $C_{13}H_{18}O_6Ag_2$; we were thus, in the first instance, led to suppose that hydrolysis had not been complete, and that this substance was the ethyl dihydrogen salt of the acid,

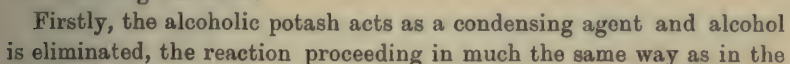
$$Me_2C\begin{<}C(CO_2H)\cdot CHEt\cdot CO_2H\\CH\cdot CO_2H\end{>}.$$

Since, however, prolonged boiling with caustic alkalis did not further hydrolyse the substance, we were obliged to abandon this view, and further investigation has led us to the conclusion that this remarkable compound is *ethoxydimethylethylketopentamethylenedicarboxylic acid*,

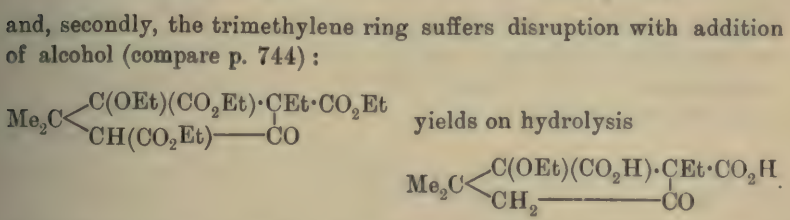


The formation of such a substance may be assumed to be the result of the following reactions.

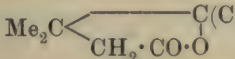
Firstly, the alcoholic potash acts as a condensing agent and alcohol is eliminated, the reaction proceeding in much the same way as in the formation of the yellow sodium compound (p. 736) :



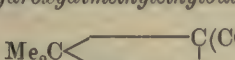
and, secondly, the trimethylene ring suffers disruption with addition of alcohol (compare p. 744) :



Remarkable as this reaction undoubtedly is, we do not see any other way of explaining the composition and properties of the substance melting at 175°. The mother liquors of this substance yield, on extraction with ether, small quantities of two acids melting at 193° with decomposition, and at 213° without decomposition ; these can be separated by means of their barium salts. Analysis shows that the former has the formula $C_{12}H_{26}O_8$, and the results of titration prove conclusively that it is a tribasic lactonic acid ; there can thus be little doubt that it is the *lactone* of *hydroxydimethylethylbutanetetracarboxylic acid*,



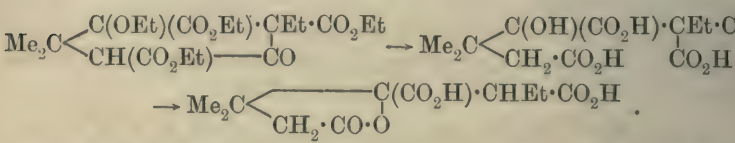
The substance of melting point 213° is a dibasic lactonic acid, $C_{11}H_{16}O_6$, and therefore very probably one of the stereoisomeric modifications of the *lactone* of *hydroxydimethylethylbutanetricarboxylic acid*,



and as it shows little tendency to form an anhydride, and melts higher than the isomeride to be mentioned immediately, we have provisionally named it *trans-*.

Although the ethoxypentamethylene derivative of melting point

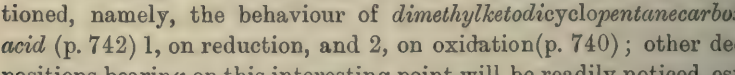
175° is so stable towards alkalis, it is readily attacked by boiling concentrated hydrochloric acid, with formation of a beautifully crystalline lactone dibasic acid, $C_{11}H_{16}O_6$, which melts at 153°, and is evidently the *cis*-modification of the *lactone* of *hydroxydimethylethylbutanetricarboxylic acid*. The formation of this dibasic lactonic acid is readily understood, if the constitution of the substance melting at 175°, which is given above, is accepted, and indeed this decomposition was one of the strong reasons which induced us to adopt this constitution.



When heated a little above its melting point, or when treated with acetyl chloride, the dibasic lactonic acid melting at 153° is readily converted into its anhydride, $C_{11}H_{14}O_5$, which on boiling with water again regenerates the same acid; for this reason, we have named this substance the *cis*-modification.

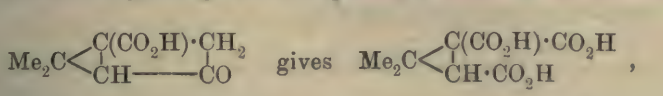
*Stability of the Ketodi*cyclo*pentane Ring, especially as compared with that of the Trimethylene Ring.*

The study of the action of reagents on the carboxylic acids of dimethylketodi*cyclo*pentane has brought to light some remarkable changes which show the instability of a bridged ring of this nature under conditions which do not usually lead to the disruption of a saturated ring. In this connection, two reactions only need be mentioned, namely, the behaviour of *dimethylketodi*cyclo*pentanecarboxylic acid* (p. 742) 1, on reduction, and 2, on oxidation (p. 740); other decompositions bearing on this interesting point will be readily noticed, especially in reading the experimental part of this paper. It has already been mentioned that dimethylketodi*cyclo*pentanecarboxylic acid is very readily reduced, and the first stage of the process is the following:

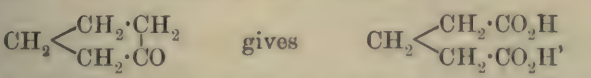


that is to say, disruption of the trimethylene ring actually takes place before the reduction of the ketonic group, and this seems to us to show that in forming a bridge in the *cyclo*pentane (pentamethylene) ring, the strain produced is so great that nascent hydrogen at the ordinary temperature is able to bring about its dissolution. The unstable nature of the bridge is further emphasised by the study of the behaviour of dimethylketodi*cyclo*pentanecarboxylic acid on oxidation,

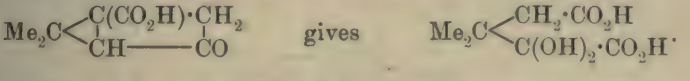
when, instead of yielding, as we expected, a trimethylene derivative, thus :



a reaction which would be exactly analogous to the formation of glutaric acid by the oxidation of ketopentamethylene,

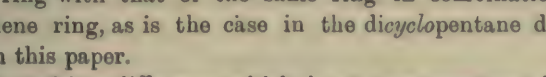


the reaction proceeds with disruption of the trimethylene ring and formation of $\alpha\alpha$-dihydroxydimethylglutaric acid,

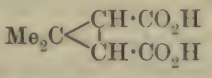


The stability of the trimethylene ring has been made the subject of much investigation, and it is interesting to contrast the stability of the simple ring with that of the same ring in combination with a tetramethylene ring, as is the case in the di*cyclo*pentane derivatives described in this paper.

The most striking difference which is at once apparent is the fact that the trimethylene ring exhibits an unusual degree of stability towards reducing and oxidising agents. Thus, the trimethylenedicarboxylic acids,



are neither oxidised by permanganate nor reduced when treated with sodium amalgam, and in describing the caronic acids,



(which are more closely allied to the substances described in this paper), Baeyer and Ipatieff (*Ber.*, 1896, **29**, 2798—2800) particularly emphasise their great stability towards oxidising and reducing agents. It is obvious, then, that the simple trimethylene ring is much more stable than the three-carbon ring in di*cyclo*pentane, and this we consider may be well explained by the assumption that in the latter hydrocarbon the bridge is produced under great strain, and therefore easily suffers disruption when treated with suitable reagents.

From this it follows that, in many cases, it will not be possible to predict, with any degree of certainty, the properties of a polycyclic compound from the consideration of the stability of the rings of which it is composed. Indeed, this is already apparent from the study of

many of the reactions of those members of the terpene series which are supposed to contain dicyclic rings.

During the course of our investigation of the derivatives of di*cyclo*pentane, we have had occasion to prepare and examine some interesting derivatives of *ββ*-dimethylglutaric acid, $CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$, and the results of these experiments may conveniently be briefly summarised as follows:

$a a_1$-Dibromodimethylglutaric acid, $CO_2H{\cdot}CHBr{\cdot}CMe_2{\cdot}CHBr{\cdot}CO_2H$, is obtained by treating dimethylglutaric acid with phosphorus pentachloride and bromine and digesting the product with anhydrous formic acid. It melts at 187—189°, and when treated with pyridine or boiled with water it yields the *lactone* of *α-bromo-a_1-hydroxy-ββ-dimethylglutaric acid*.

$$Me_2C\begin{cases}CHBr\text{———}CO\\ CH(CO_2H){\cdot}O\end{cases}.$$

This melts at 169—170°, gives an ethyl ester boiling at 201° under 45 mm. pressure, and is characterised by the great stability of its bromine atom, which is not removed by boiling with silver nitrate and nitric acid. When, however, the bromolactone is boiled with strong potash, it yields the corresponding *lactone* of *$a a_1$-dihydroxy-ββ-dimethylglutaric acid*,

$$Me_2C\begin{cases}CH(OH)\text{—}CO\\ CO(CO_2H){\cdot}O\end{cases},$$

which melts at 142°, and seems to have little tendency to form a double lactone.

When *ββ-dimethylglutaric acid* is brominated, the principal product is the $a a_1$-dibromo-acid mentioned above, but, at the same time, a small quantity of the *aa*-dibromo-acid, $CO_2H{\cdot}CBr_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$, is always formed, and on pouring the product of bromination into alcohol, the former is completely converted into the diethyl ester, whereas the latter yields, curiously enough, only the ethyl hydrogen salt which probably has the composition $CO_2H{\cdot}CBr_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2Et$.

This, when boiled with sodium carbonate, yields *aa-dihydroxydimethylglutaric acid*, an acid which, as has already been mentioned (p. 757), had been obtained in quite a different way, namely, by the oxidation of dimethylketodi*cyclo*pentanecarboxylic acid; the formation of the *aa*-dibromo-acid in the above example leads us to expect that when other dibasic acids containing two CH_2 groups (or a CH_2 and a CH group) next the carboxyl groups are brominated, besides the $a a_1$-dibromo-acid, which is probably in all cases the principal product of the reaction, a certain quantity of the *aa*-dibromo-acid will also be found to be produced.

Thus, in the case of the bromination of succinic acid, for

example, the product may very probably consist of the two acids $CO_2H\cdot CHBr\cdot CHBr\cdot CO_2H$ and $CO_2H\cdot CBr_2\cdot CH_2\cdot CO_2H$, the latter being present in such small quantity that it has so far been overlooked.

In publishing this paper, we do so in order to place on record the mass of facts which has gradually accumulated, but we are, nevertheless, well aware that there is still much that is doubtful, particularly in regard to the constitutions of the various lactones described. We hope at a later date, as the result of further experimental investigation, to be able to clear up these difficulties.

During the four years which were required for carrying out this investigation, we have received most valuable help from Messrs. F. H. Lees and J. Yates, to the latter of whom, especially, most of the analyses given in this paper are due. Our thanks are also due to Mr. C. Walker for his assistance in the preparation of a considerable quantity of the necessary material.

We wish also to state that much of the heavy expense, which is unavoidable in an investigation of this kind, has been met by repeated grants from the Government Grant Fund of the Royal Society.

Experimental.

Part I. Derivatives of ββ-Dimethylglutaric Acid: Formation of Ethyl Dimethyltrimethylenemalonate and its Derivatives.

By W. H. Perkin, jun., and J. F. Thorpe.

Preparation of ββ-Dimethylglutaric Anhydride, $Me_2C\langle\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}\rangle O$. —When ethyl sodiocyanoacetate is condensed in alcoholic solution, with ethyl dimethylacrylate, the product consists for the most part of ethyl hydrogen α-cyano-ββ-dimethylglutarate,

$$CO_2H\cdot CH(CN)\cdot CMe_2\cdot CH_2\cdot CO_2Et,$$

which is converted by hydrolysis with sulphuric acid into ββ-dimethylglutaric acid (Trans., 1899, 75, 52, 54).

In preparing, from the ethyl hydrogen cyano-ester, the large quantities of dimethylglutaric anhydride which were necessary for this research, we found the following process to give the best results.

The crude cyano-ester is heated with twice its volume of 50 per cent. sulphuric acid until all oil has passed into solution, the operation being conducted in a flask connected with an air condenser so that the alcohol formed can escape; from time to time, small quantities of

water are added to keep the liquid at its original volume. The product is mixed with a saturated solution of ammonium sulphate, extracted several times with ether, the ethereal solution dried over calcium chloride and evaporated, when a dark brown, crystalline cake of crude dimethylglutaric acid is obtained. This is boiled with an equal volume of acetic anhydride for 2 hours; the acetic acid and the excess of acetic anhydride are then distilled off as far as possible under the ordinary pressure and the residue fractionated under 30 mm. pressure, when almost the whole of the anhydride passes over at 180—190°, and immediately solidifies in the receiver. In order to further purify this, advantage is taken of the fact that the anhydride is sparingly soluble in dry ether, so that, if the crude product is ground up with dry ether, the impurities dissolve, leaving a residue of colourless crystals of the pure anhydride.

The impurities extracted by the ether contain nitrogen, and after distilling off the ether, the residue is again boiled with dilute sulphuric acid and the whole process repeated as given above, when a further considerable quantity of pure anhydride is easily obtained. The properties of this compound have already been given (Trans., 1896, **69**, 1475).

Bromination of ββ-Dimethylglutaric Anhydride. Formation of Ethyl $a a_1$*-Dibromo-ββ-dimethylglutarate,* $CO_2Et\cdot CHBr\cdot CMe_2\cdot CHBr\cdot CO_2Et$, *and Ethyl Hydrogen aa-Dibromo-ββ-dimethylglutarate,*

$$CO_2H\cdot CBr_2\cdot CMe_2\cdot CH_2\cdot CO_2Et\ (?).$$

As mentioned in the introduction, *ββ*-dimethylglutaric anhydride, when treated with phosphorus and bromine, is both symmetrically and unsymmetrically brominated, the proportions of the former product to the latter being approximately five to one. The conditions under which we always carried out this bromination were as follows.

Pure dimethylglutaric anhydride (100 grams) was mixed with 300 grams of phosphorus pentabromide and the mixture warmed on the water-bath until all had become liquid. Bromine (225 grams) was then gradually added and the whole heated on the water-bath until nearly colourless, a process lasting usually from 5—6 hours. The product, after cooling, was poured into four times its volume of absolute alcohol and the whole allowed to stand for 12 hours. The oil, which separated on adding water, was extracted with ether, washed with water and dilute sodium carbonate, and dried over calcium chloride. The ethereal solution on evaporating yielded 216 grams of *ethyl* $a a_1$*-dibromodimethylglutarate* as a colourless liquid boiling at 194° under 30 mm. pressure.

0·5336 gram gave 0·4213 AgBr. Br = 42·53.

$C_{11}H_{18}O_4Br_2$ requires Br = 42·79 per cent.

The sodium carbonate washings of the ethereal solution (see above) on acidifying gave a thick oil; this was extracted with ether, the ethereal solution washed with water, dried over calcium chloride, and evaporated, when an oil was obtained which, from the results of analysis and its behaviour on boiling with sodium carbonate, is evidently *ethyl hydrogen αα-dibromo-ββ-dimethylglutarate*; it is a thick oil which does not distil without decomposition.

0·1976 gram gave 0·2134 AgBr. Br = 46·5.

$C_9H_{14}O_4Br_2$ requires Br = 46·2 per cent.

The constitution of this substance is proved by its conversion into $\alpha\alpha_1$-dihydroxydimethylglutaric acid, $CO_2H{\cdot}C(OH)_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$, by treatment with sodium carbonate (p. 757).

αα$_1$-Dibromo-ββ-dimethylglutaric Acid, $CO_2H{\cdot}CHBr{\cdot}CMe_2{\cdot}CHBr{\cdot}CO_2H$ is best prepared in the following way. The dibromo-acid bromide, prepared by brominating dimethylglutaric anhydride with the theoretical quantity of bromine and phosphorus pentabromide, as explained above, is poured into an equal volume of glacial formic acid, and the mixture heated on the water-bath until all has dissolved. On cooling, a large quantity of a crystalline solid separates, which can be collected and recrystallised from glacial formic acid, from which it is obtained in the form of large, colourless prisms melting at 187—189° with charring and evolution of gas.

0·1827 gave 0·2129 AgBr. Br = 49·9.

$C_7H_{10}O_4Br_2$ requires Br = 50·2 per cent.

Dibromodimethylglutaric Acid is readily soluble in hot water and separates from the solution unchanged if the operation is rapidly conducted, but since on boiling with water it is gradually decomposed with formation of the lactone of bromohydroxydimethylglutaric acid (see below), it is best to recrystallise it from formic acid.

Lactone of α-Bromo-α$_1$-hydroxy-ββ-dimethylglutaric Acid,

$$Me_2C\begin{cases}CHBr\text{——}CO\\ CH(CO_2H){\cdot}O\end{cases},$$

When dibromodimethylglutaric acid is mixed with excess of pyridine, a considerable development of heat occurs, and if the solution is boiled for two minutes, then cooled, and poured into excess of hydrochloric acid, the above lactone is obtained as a white, crystalline mass on extracting with ether. The same bromolactone is also gradually formed when the dibromo-acid is boiled with water, complete decomposition of the dibromo-acid being brought about after boiling for 12 hours.

Since, however, the bromolactone, during this process, undergoes further change and is partially converted into the hydroxylactone (see below), the pyridine method of preparation is to be preferred. The same bromolactone is also formed when dibromodimethylglutaric acid suspended in water is treated with moist silver oxide.

The *lactone of bromohydroxydimethylglutaric acid* separates from hot water, in which it is readily soluble, in large, transparent prisms and melts at 169—170°. It is a remarkably stable substance which distils unchanged and is unacted on by fuming nitric acid, or by boiling for 12 hours with pyridine.

0·1811 gave 0·2373 CO_2 and 0·0678 H_2O. C = 35·7; H = 4·1.
0·1919 „ 0·2459 CO_2 „ 0·0690 H_2O. C = 35·0; H = 4·0.
$C_7H_9O_4Br$ requires C = 35·4. H = 3·8 per cent.

Since no trace of silver bromide was formed when this bromolactone was boiled with fuming nitric acid and nitrate of silver, the substance was analysed for bromine by fusing it with potassium nitrate and carbonate.

0·2113 gave 0·1659 AgBr. Br = 33·5.
$C_7H_9O_4Br$ requires Br = 33·7 per cent.

The *ethyl* ester, $Me_2C<\begin{matrix}CHBr\text{——}CO\\ CH(CO_2Et)\cdot O\end{matrix}$, is readily obtained by boiling the alcoholic solution of the bromolactone with 10 per cent. of concentrated sulphuric acid on the water-bath for 12 hours. It is a mobile oil which distils without decomposition at 201° under 45 mm. pressure.

0·1778 gave 0·2698 CO_2 and 0·0846 H_2O. C = 41·3; H = 5·2.
0·3421 „ 0·2417 AgBr. Br = 30 1.
$C_9H_{13}O_4Br$ requires C = 40·7; H = 4·9; Br = 30·2 per cent.

Lactone of $\alpha\alpha_1$-Dihydroxy-$\beta\beta$-dimethylglutaric Acid,

$$Me_2C<\begin{matrix}CH(OH)\text{—}CO\\ CH(CO_2H)\cdot O\end{matrix},$$

Although the bromolactone just described is extremely stable towards acids, it is readily acted on by alkalis, and boiling for 2 hours with a 25 per cent. solution of aqueous potash is sufficient to completely transform it into the above lactone. This compound is very soluble in water; it distils without decomposition, and on warming with concentrated sulphuric acid evolves carbon monoxide. For analysis, the substance was crystallised from dry ether, from which it separates in long needles melting at 140—142°.

0·1682 gave 0·2967 CO_2 and 0·0884 H_2O. C = 48·1 ; H = 5·8.
$C_7H_{10}O_5$ requires C = 48·3 ; H = 5·7 per cent.

The *silver* salt, $C_7H_{10}O_6Ag_2$, of the dihydroxy-acid is obtained when silver nitrate is added to a warm neutral solution of the lactone in ammonia, as a white, crystalline powder moderately soluble in water,

0·3522 gave 0·1866 Ag. Ag = 52·8.
$C_7H_{10}O_6Ag_2$ requires Ag = 53·0 per cent.

When calcium chloride is added to the neutral solution of the ammonium salt, an insoluble calcium salt is thrown down, which may with advantage be used for the isolation of the lactone of the dihydroxy-acid from mixtures with other substances.

αα-Dihydroxy-ββ-dimethylglutaric Acid,
$CO_2H\cdot C(OH)_2\cdot CMe_2\cdot CH_2\cdot CO_2H$.

When ethyl hydrogen αα-dibromodimethylglutarate (p. 755) is dissolved in sodium carbonate solution and boiled, care being taken to keep the solution faintly alkaline throughout the process, it is found that, after 2 hours, no oil is precipitated on acidifying.

If the acidified solution is then saturated with ammonium sulphate and repeatedly extracted with ether, a gummy acid is obtained from the ethereal solution on evaporation which, when dissolved in excess of ammonia and mixed with calcium chloride solution, slowly deposits a large quantity of a crystalline calcium salt. On washing this salt, decomposing it with hydrochloric acid, and extracting with ether, a solid acid is obtained which crystallises from chloroform in long, silky needles and melts at 84°. It is extremely soluble in water, ether, or ethyl acetate, but only sparingly so in benzene, and is almost insoluble in light petroleum.

0·1607 gave 0·2618 CO_2 and 0·0931 H_2O. C = 44·4 ; H = 6·3.
$C_7H_{12}O_6$ requires C = 43·8 ; H = 6·3 per cent.

The *silver* salt, $C_7H_8O_5Ag_2$, is precipitated as a white, crystalline powder on adding silver nitrate to a neutral solution of the ammonium salt. It explodes when heated. Analysis shows that it is the silver salt of the ketonic acid, $CO_2Ag\cdot CO\cdot CMe_2\cdot CH_2\cdot CO_2Ag$.

0·2516 gave 0·1395 Ag. Ag = 55·44.
$C_7H_8O_5Ag_2$ requires Ag = 55·6 per cent.
$C_7H_{10}O_6Ag_2$ „ Ag = 53·2 „

The *calcium* salt, $C_7H_{10}O_6Ca$, is characteristic, and separates slowly in the form of needles from a slightly alkaline solution of the ammonium salt on the addition of calcium chloride.

Condensation Product with o-Tolylenediamine;

$$CO_2H\cdot CH_2\cdot CMe_2\cdot \overset{\displaystyle CO-NH}{\overset{|}{\underset{|}{C}}}\cdot N\cdot C_6H_3\cdot CH_3$$

—When a clear solution of *o*-tolylenediamine hydrochloride was mixed with sodium acetate and added to an aqueous solution of the acid and the whole boiled for a few minutes and allowed to stand, a crystalline precipitate separated which, after recrystallising from water, gave the following results on analysis:

0·2013 gave 0·4772 CO_2 and 0·1135 H_2O. C = 64·6; H = 6·3.
0·1582 „ 0·3755 CO_2 „ 0·0895 H_2O. C = 64·7; H = 6·3.
0·1810 „ 17·2 c.c. nitrogen at 21° and 770 mm. N = 10·96.
$C_{14}H_{16}O_3N_2$ requires C = 64·6; H = 6·1; N = 10·8 per cent.

There can scarcely be a doubt that the constitution of this condensation product is that represented by the formula given above, and it is quite possible that other *α*-ketonic acids will be found to react with *o*-tolylenediamine and other *o*-diamines in the same way, yielding condensation products which may prove valuable as a means of diagnosing the nature of such acids.

Lactone of α-Hydroxy-ββ-dimethylglutaric Acid,

$$\overset{\displaystyle CO\text{———}O}{\overset{|}{\underset{|}{CH_2}}}\cdot CMe_2\cdot CH\cdot CO_2H$$

In preparing this lactone, 5 grams of pure dihydroxydimethylglutaric acid (see previous section) were dissolved in sodium carbonate solution, and treated with excess of sodium amalgam in the cold; a stream of carbon dioxide being led into the solution during the process. After standing overnight, the solution was evaporated to a small bulk, acidified, and repeatedly extracted with ether, when on evaporating off the ether a solid substance remained, which was purified by treating the solution in water with excess of ammonia, evaporating to dryness, and extracting the well dried solid ammonium salt with absolute alcohol. The alcoholic solution after filtering and mixing with four times its bulk of dry ether, gradually deposited small prisms of an ammonium salt, which were collected, decomposed with dilute hydrochloric acid, and the solution extracted with ether. The solid lactone which remained after distilling off the ether was readily crystallised from a small quantity of water, from which it separated in glistening prisms, and these, after standing on a piece of porous plate exposed to the air for a week, furnished the following numbers on analysis:

0·0988 gave 0·1740 CO_2 and 0·0614 H_2O. C = 48·0; H = 6·9.
$C_7H_{10}O_4,H_2O$ requires C = 47·8; H = 6·8 per cent.

This substance, which consists therefore of the lactone crystallising

with 1 mol. of water, melts indefinitely between 50° and 80°, at the same time giving up its water of crystallisation. In a vacuum desiccator over sulphuric acid, the hydrated crystals soon become opaque owing to loss of water, and the dehydrated substance then melts at 112° and consists of the pure lactone of α-hydroxydimethylglutaric acid.

0·1586 gave 0·3103 CO_2 and 0·0909 H_2O. C = 53·3 ; H = 6·4.
$C_7H_{10}O_4$ requires C = 53·2 ; H = 6·3 per cent.

This lactone is identical in all its properties with the lactone prepared by us (Trans., 1899, **75**, 56) by the action of sodium carbonate on ethyl hydrogen α-bromo-ββ-dimethylglutarate,

$$CO_2H\cdot CHBr\cdot CMe_2\cdot CH_2\cdot CO_2H,$$

but at that time it was not noticed that the lactone possessed the property of crystallising with water.

The rather remarkable property of a lactone crystallising with water without being converted into the hydroxy-acid has been observed before. Thus, Baeyer and Villiger (*Ber.*, 1897, **30**, 1955) showed that the β-lactone of dimethylmalic acid crystallises in prisms of the formula $C_6H_8O_4,H_2O$, and, as other examples, terpenylic acid and the lactones of hydroxycamphoronic acid, all of which crystallise with water, may be cited.

Action of Ethyl Alcoholic Potash on Ethyl αα₁-Dibromo-ββ-dimethylglutarate. Formation of Ethoxycaronic Acid, $Me_2C<\begin{matrix}C(OEt)\cdot CO_2H\\ |\\ CH\cdot CO_2H\end{matrix}$.

The action of alcoholic potash on this dibromo-ester was studied with the view of preparing an acid of the formula $Me_2C<\begin{matrix}C\cdot CO_2H\\ ||\\ C\cdot CO_2H\end{matrix}$ the ethyl ester of which, as stated in the introduction, we considered to be an intermediate product in the formation of the yellow sodium compound (p. 732). We were, however, unable to obtain this unsaturated acid by this reaction, owing to the readiness with which it adds on alcohol to form ethoxycaronic acid.

The hydrolysis was accomplished by heating equal weights of the bromo-ester and potash (dissolved in ethyl alcohol) for 3 hours on the water-bath, and then evaporating off the alcohol. The residue was dissolved in water, acidified, and extracted with ether in the usual way. The semi-solid mass which remained after distilling off the ether, yields a crystalline acid on rubbing with concentrated hydrochloric acid ; this was collected and purified by crystallisation from benzene.

0·1871 gave 0·3662 CO_2 and 0·1174 H_2O. C = 53·4; H = 7·0.
0·1659 „ 0·3255 CO_2 „ 0·1036 H_2O. C = 53·5; H = 7·0.
$C_9H_{14}O_5$ requires C = 53·4; H = 6·9 per cent.

Ethoxycaronic acid crystallises from benzene or water in long needles and melts at 138°; it is readily soluble in water, alcohol, or hot benzene, but only sparingly so in light petroleum.

One of its most characteristic salts is the *calcium* salt, which separates as a sparingly soluble crystalline precipitate on heating a neutral solution of the ammonium salt with calcium chloride.

The *silver* salt, $C_9H_{12}O_5Ag_2$, separates from a neutral solution of the ammonium salt on the addition of silver nitrate as a white, amorphous precipitate.

0·3195 gave 0·1652 Ag. Ag = 51·7.
$C_9H_{12}O_5Ag_2$ requires Ag = 51·8 per cent.

Ethoxycaronic Anhydride, $Me_2C<\begin{matrix}C(OEt)\cdot CO\\ |\\ CH\text{——}CO\end{matrix}>O$, is formed either when the acid is distilled under the ordinary pressure, or better, when it is heated with acetic anhydride and the product distilled.

It is a colourless oil which distils at 160—165° under 50 mm. pressure, and on boiling with water is again converted into ethoxycaronic acid.

0·1860 gave 0·3988 CO_2 and 0·1107 H_2O. C = 58·5; H = 6·6.
$C_9H_{12}O_4$ requires C = 58·6; H = 6·5 per cent.

Action of Sodium Ethoxide on Ethyl $a a_1$*-Dibromodimethylglutarate. Formation of Ethyl Ethoxycaronate*, $Me_2C<\begin{matrix}C(OEt)\cdot CO_2Et\\ |\\ CH\cdot CO_2Et\end{matrix}$.

This reaction was studied in order to show that the first action of sodium ethoxide on the dibromo-ester is to eliminate 2 mols. of hydrogen bromide, forming an unsaturated ester, $Me_2C<\begin{matrix}C\cdot CO_2Et\\ ||\\ C\cdot CO_2Et\end{matrix}$, which then either reacts with the alcohol present to form ethyl ethoxycaronate, or condenses with any other suitable substance, such as ethyl malonate, which may be present in the solution (p. 732).

Ethyl $a a_1$-dibromodimethylglutarate was digested with the theoretical quantity of sodium dissolved in alcohol, and the mixture heated on the water-bath until neutral. Water was then added, and the oil which separated, extracted with ether and fractionated under diminished pressure, when almost the whole quantity distilled at 160° under 35 mm. pressure as a colourless oil.

0·1866 gave 0·4055 CO_2 and 0·1412 H_2O. C = 59·3; H = 8·4.
$C_{13}H_{22}O_5$ requires C = 60·5; H = 8·5 per cent.

The rather low figures are accounted for by the fact that the substance contained a trace of bromine. That it was ethyl ethoxycaronate was proved by its behaviour on hydrolysis. The oil was heated for 2 hours with an equal weight of potash dissolved in alcohol, the alcohol removed by evaporation, and the residue acidified and extracted with ether, when on distilling off the ether a gum was obtained which gradually solidified. After crystallising twice from benzene, long colourless needles were obtained, which melted at 138° and consisted of pure *ethoxycaronic acid.*

0·1807 gave 0·3536 CO_2 and 0·1127 H_2O. C = 53·4 ; H = 6·9.
$C_9H_{14}O_5$ requires C = 53·5 ; H = 6·9 per cent.

The yield of ethyl ethoxycaronate obtained in the above experiment was 90 per cent. of the theoretical, and this method, therefore, affords a convenient way of obtaining this ester in quantity.

In the hope of being able to split off alcohol from ethyl ethoxycaronate, and then obtain the unsaturated ester, $Me_2C<^{C\cdot CO_2Et}_{C\cdot CO_2Et}$, a quantity of the pure ester was heated to boiling for an hour under the ordinary pressure in a small distillation flask inclined so as to allow the oily liquid of high boiling point to flow back. On subsequent distillation, the whole passed over at 240°, and proved to be the unchanged ester.

0·1489 gave 0·3309 CO_2 and 0·1155 H_2O. C = 60·6 ; H = 8·6.
$C_{13}H_{22}O_5$ requires C = 60·5 ; H = 8·5 per cent.

Methoxycaronic Acid, $Me_2C<^{C(OMe)\cdot CO_2H}_{CH\cdot CO_2H}$.

When ethyl $\alpha\alpha_1$-dibromodimethylglutarate is digested with an equal weight of potash dissolved in methyl alcohol for 2 hours, it is completely hydrolysed and on evaporating, acidifying, and extracting with ether, a semi-solid mass is obtained which, when rubbed with cold hydrochloric acid, yields a quantity of crystals of methoxycaronic acid. These were collected and recrystallised from dilute hydrochloric acid, from which the substance separates in small prisms.

0·1867 gave 0·3507 CO_2 and 0·1081 H_2O. C = 51·2 ; H = 6·4.
$C_8H_{12}O_5$ requires C = 51·1 ; H = 6·4 per cent.

Methoxycaronic acid melts at 148°, and, when distilled, water is eliminated, and the acid converted into the *anhydride*, a colourless liquid boiling at 169° under 33 mm. pressure.

0·2164 gave 0·4821 CO_2 and 0·1149 H_2O. C = 56·7 ; H = 5·9.
$C_8H_{10}O_4$ requires C = 56·5 ; H = 5·9 per cent.

On boiling this anhydride with water, it is slowly reconverted into methoxycaronic acid.

Action of Sulphuric Acid and of Hydrobromic Acid on Ethoxy- and Methoxy-caronic Acids. Formation of αα-Dimethylsuccinic Acid, $CO_2H\cdot CMe_2\cdot CH_2\cdot CO_2H$, *and of αα-Dihydroxy-ββ-dimethylglutaric Acid,* $CO_2H\cdot C(OH)_2\cdot CMe_2\cdot CH_2\cdot CO_2H$.

When ethoxycaronic acid or methoxycaronic acid is heated with concentrated sulphuric acid at 100°, a rapid evolution of carbon monoxide ensues, and the liquid now contains αα-dimethylsuccinic acid, a curious decomposition, for which an explanation is given in the introduction. After the evolution of gas had ceased, the product was cooled, mixed with twice its volume of water, saturated with ammonium sulphate, and extracted several times with ether. The ethereal solution was dried and evaporated, when a solid acid was obtained which crystallised from hydrochloric acid in needles melting at 139—140°, and showed all the properties of *αα-dimethylsuccinic acid.*

0·1795 gave 0·3242 CO_2 and 0·1111 H_2O. C = 49·2; H = 6·9.
$C_6H_{10}O_4$ requires C = 49·3; H = 6·8 per cent.

The solution of this acid in a slight excess of ammonia gave, on boiling with calcium chloride, the characteristic calcium salt of dimethylsuccinic acid; and a quantity of the acid, after boiling with acetyl chloride and distillation, yielded the anhydride of dimethylsuccinic acid melting at 29°.

When either ethoxy- or methoxy-caronic acid is heated with concentrated hydrobromic acid in a sealed tube at 100° for 5 hours, it is quantitatively converted into αα-dimethylsuccinic acid.

If, however, the action of hydrobromic acid is first allowed to take place in the cold, that is to say, if the mixture of the ethoxy- or methoxy-acid and hydrobromic acid (saturated at 0°) is allowed to stand for 12 hours at the ordinary temperature and then evaporated on the water-bath, the product consists of an unstable bromo-acid which is evidently αα-dibromodimethylglutaric acid,

$$CO_2H\cdot CBr_2\cdot CMe_2\cdot CH_2\cdot CO_2H,$$

since on boiling with water it is quantitatively converted into αα-dihydroxydimethylglutaric acid, $CO_2H\cdot C(OH)_2\cdot CMe_2\cdot CH_2\cdot CO_2H$.

The acid thus obtained crystallised from chloroform in needles melting at 84° and a direct comparison showed that it was identical with the dihydroxy-acid prepared by the action of sodium carbonate on ethyl hydrogen αα-dibromodimethylglutarate, and described on p. 757.

0·1577 gave 0·2541 CO_2 and 0·0920 H_2O. C = 43·9; H = 6·4.
0·1713 „ 0·2751 CO_2 „ 0·0991 H_2O. C = 43·8; H = 6·4.
$C_7H_{12}O_6$ requires C = 43·8; H = 6·2 per cent.

Action of Ethyl Dibromodimethylglutarate on Ethyl Sodiomalonate. Formation of Ethyl Dicarboxydimethyltrimethylenemalonate,

$$Me_2C<\begin{matrix}C(CO_2Et)\cdot CH(CO_2Et)_2\\ CH\cdot CO_2Et\end{matrix}.$$

For reasons explained in the introduction, and in order that this process, which lies at the base of the formation of the di*cyclo*pentane compounds described in this paper, should be thoroughly understood, the reaction was carried out under varied conditions, two of which may be described in detail.

Experiment I.—The proportions used were: ethyl malonate (2 mols.), sodium (2 at.), and ethyl dibromodimethylglutarate (1 mol.). The sodium (5 grams) was dissolved in 60 grams of absolute alcohol, mixed when nearly cold with the ethyl malonate (36 grams), and then with the dibromo-ester (40 grams). On heating the mixture on the water-bath, sodium bromide soon began to separate, and at the end of an hour the reaction was finished. The deep yellow product was washed with water and with dilute sodium carbonate, dried over calcium chloride, and evaporated, when 62 grams of an oil containing only traces of bromine were obtained. On distilling this under 30 mm. pressure, about 20 grams passed over below 135°, and consisted principally of ethyl malonate. The thermometer then rose rapidly to 215°, almost the whole of the residue passing over between this and 230°. Some of this fraction was redistilled, and the portion boiling at 222° under 30 mm. pressure analysed.

0·1511 gave 0·3191 CO_2 and 0·1055 H_2O. C = 57·6; H = 7·7.
$C_{18}H_{28}O_8$ requires C = 58·0; H = 7·5 per cent.

This ester gave, on hydrolysis, the lactones of the hydroxydimethylbutanetricarboxylic acids (p. 764), and when treated with sodium ethoxide and ethyl iodide it was converted into ethyl dicarboxyethyldimethyltrimethylenemalonate (p. 770); there can therefore be no doubt that it is *ethyl dicarboxydimethyltrimethylenemalonate*, and has the constitution represented by the formula at the head of this section.

Experiment II.—The proportions used were approximately 21 grams of ethyl malonate (1 mol.), 6 grams of sodium (2 at.), and 47 grams of ethyl dibromodimethylglutarate (1 mol.). The details of the carrying out of the reaction and isolation of the product were the same as in Expt. I. The 45 grams of neutral oily product obtained distilled, for

the most part, at 222—225° under 30 mm. pressure, and furnished the following results on analysis :

0·1366 gave 0·288 CO_2 and 0·0952 H_2O. C = 57·7 ; H = 7·7.
$C_{18}H_{28}O_8$ requires C = 58·0 ; H = 7·5 per cent.

A small quantity of this oil, on hydrolysis, yielded the same products as in the case of the ester obtained in Expt. I, so that it also must be *ethyl dicarboxydimethyltrimethylenemalonate.*

Hydrolysis of Ethyl Dicarboxyldimethyltrimethylenemalonate. Formation of the Lactones of A- and B-Hydroxydimethylbutanetricarboxylic Acids, $Me_2C<\begin{matrix}C(CO_2H)\cdot CH_2\cdot CO_2H\\ CH_2\cdot CO\cdot O\end{matrix}$, and

$$Me_2C<\begin{matrix}CH(CH_2\cdot CO_2H)\\ CH(CO_2H)\end{matrix}>CO.$$

When equal weights of the ethyl ester and potash are dissolved in methyl alcohol, a deep yellow solution is formed, which, on heating, gradually loses its yellow colour, and is completely hydrolysed after boiling for 2 hours. Water is now added, and the solution, after evaporating until quite free from methyl alcohol, and then acidifying, is saturated with ammonium sulphate and extracted at least 20 times with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposits a thick, brown oil, which on standing becomes semi-solid ; in contact with porous porcelain, most of the oily matter is absorbed in about a week, leaving a brown, crystalline mass weighing about one-third of the ester employed in the hydrolysis. When this crude mass is ground up with cold water, about half dissolves, and on filtering on the pump an ochre-coloured substance remains, which is sparingly soluble in cold water, and may be readily obtained in the form of colourless prisms by repeated recrystallisation from water with the aid of animal charcoal.

0·1376 gave 0·2522 CO_2 and 0·0698 H_2O. C = 50·0 ; H = 5·6.
0·1730 „ 0·3168 CO_2 „ 0·0884 H_2O. C = 49·9 ; H = 5·7.
$C_9H_{12}O_6$ requires C = 50·0 ; H = 5·6.

This *lactone* of *B-hydroxydimethylbutanetricarboxylic acid* melts, when rapidly heated, at about 188—190° with evolution of gas, but the melting point, which is in reality the decomposing point, varies considerably with the rate of heating.

That this substance is a dibasic acid is proved by its behaviour on titration with decinormal caustic soda, when 0·2635 gram required for neutralisation 0·1 gram NaOH. Assuming the acid to be dibasic, this quantity should have neutralised 0·098 gram NaOH ; boiling with

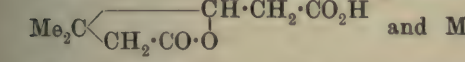
excess of decinormal soda appears to hydrolyse the lactone ring only very gradually.

The *Lactone of A-Hydroxydimethylbutanetricarboxylic Acid.*—The aqueous solution obtained by treating the crude solid product of the hydrolysis of the ester with cold water, as described above, was saturated with hydrogen chloride, taking care that the temperature did not rise above 40° during the operation. After standing for some days, the crystals which had separated were collected, washed with hydrochloric acid, * dissolved in as little water at 50° as possible, and the solution cooled with ice and well stirred, when a very small quantity of the lactone of the B-acid crystallised out. After filtering, the filtrate was saturated with hydrogen chloride as before, and the crystals, which separated on standing, were collected, drained on porous porcelain, dried at 80°, and analysed :

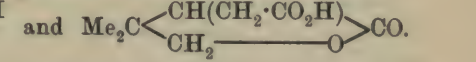
0·1581 gave 0·2836 CO_2 and 0·0819 H_2O. C = 48·9 ; H = 5·7.
0·1423 ,, 0·2586 CO_2 ,, 0·0737 H_2O. C = 49·5 ; H = 5·7.
$C_9H_{12}O_6$ requires C = 50·0 ; H = 5·6 per cent.

This lactone, when heated in a capillary tube, decomposes with evolution of gas at about 158° ; it is much more readily soluble in water than the lactone of the B-hydroxy-acid. On titration, it behaves as a dibasic acid, since 0·2398 gram required for neutralisation 0·088 gram NaOH, whereas this amount of a dibasic acid, $C_9H_{12}O_6$, should neutralise 0·086 gram NaOH.

Lactones of A- and B-Hydroxydimethylbutanedicarboxylic Acids,



and



When the lactone of B-hydroxydimethylbutanetricarboxylic acid (m. p. 188°) is heated at 190—200°, it decomposes with evolution of carbon dioxide, and in investigating this curious decomposition, we, in the first place, determined quantitatively the amount of gas produced in this way. The experiment was carried out by heating the substance to its decomposing point in a platinum boat in an empty piece of combustion tube, placed in a combustion furnace, and collecting the carbon dioxide evolved in potash bulbs, much in the same way as if an elementary analysis were being performed.

I. 0·577 gave 0·1098 CO_2. CO_2 = 19·0.
II. 0·453 ,, 0·0937 CO_2. CO_2 = 20·7.

* The mother liquors from these crystals, on evaporation at the ordinary temperature over sulphuric acid and solid potash in a vacuum desiccator, deposit a further crop of crystals of the same substance.

Assuming the reaction $C_9H_{12}O_6 = C_8H_{12}O_4 + CO_2$ to take place, the loss of carbon dioxide should be 20·4 per cent.

A portion of the residue in experiment II, after boiling with water and animal charcoal and evaporating to dryness, was analysed, with the following results:

0·113 gave 0·232 CO_2 and 0·0712 H_2O. C = 56·0; H = 6·7.

$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

so that, apparently, no decomposition other than loss of carbon dioxide takes place during this process.

About 5 grams of the pure lactone of the B-hydroxytribasic acid were now heated at 200° in a test-tube, placed in a sulphuric acid bath until all evolution of gas had ceased, and the residue, which was a thick, almost colourless, resin very readily soluble in water, was dissolved in a slight excess of dilute ammonia, and the solution mixed with calcium chloride. The crystalline, sparingly soluble calcium salt, which gradually separated on boiling, was collected on the pump, rapidly washed with hot water, decomposed with dilute hydrochloric acid and the solution repeatedly extracted with pure ether. After drying over calcium chloride and evaporating off the ether, a thick, transparent resin remained which, on standing for some weeks in a desiccator over sulphuric acid, began to crystallise in nodular masses and ultimately became quite hard. On grinding up the mass with hydrochloric acid, a trace of oily impurity was removed and the residue, after draining on porous porcelain, was a hard, colourless, crystalline substance which melted at 107—108°, and was analysed with the following results:

0·1256 gave 0·2538 CO_2 and 0·0772 H_2O. C = 55·1; H = 6·8.

$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

As these numbers were rather low, the substance was dissolved in a very little water, the solution saturated with hydrogen chloride at about 30° and allowed to stand, when hard, crystalline crusts separated, which, however, furnished a still less satisfactory result on analysis:

0·1571 gave 0·3152 CO_2 and 0·0950 H_2O. C = 54·7; H = 6·7 per cent.

It was then found that the crystals, which again melted at 108°, contained traces of chlorine, due, no doubt, to the action of the hydrochloric acid, and this accounts for the rather low analytical numbers.

The *lactone* of *B-hydroxydimethylbutanedicarboxylic acid* is very readily soluble in water, forming a strongly acid solution, which on titration takes up rather more alkali than calculated on the basis of its being a monobasic acid, showing that hydrolysis of the lactone ring takes place to a small extent at the ordinary temperature.

0·2064 gram of the acid dissolved in cold water required for neutral-

isation 0·054 gram NaOH, whereas this quantity of a monobasic acid, $C_8H_{12}O_4$, requires 0·048 gram NaOH, but if it became dibasic in solution it would neutralise 0·096 gram NaOH.

The *calcium* salt, $(C_8H_{11}O_4)_2Ca,4H_2O$ (?), obtained as described above, and dried at 100°, was analysed:

0·2300 gave 0·1026 $CaSO_4$. Ca = 13·1 per cent.

A different sample of the salt was prepared from the acid melting at 108° by boiling with excess of calcium chloride and ammonia. The crystalline crusts which separated were well washed with hot water, dried at 100°, and analysed, with the same result as before:

0·1303 gave 0·057 $CaSO_4$. Ca = 13·2 per cent.

These numbers agree well with the formula $(C_8H_{11}O_4)_2Ca,4H_2O$, which requires Ca = 13·3 per cent., but this formula must remain doubtful until an actual determination of the water of crystallisation has been made. It is, however, worthy of note that other calcium salts of similarly constituted lactonic acids are known which contain water of crystallisation, and do not become anhydrous at 100°. Thus, for example, the calcium salt of the lactone of α-hydroxydimethyltricarballylic acid (Baeyer, *Ber.*, 1896, **29**, 2795) has the formula $C_8H_8O_6Ca,3H_2O$, and still contains 1 mol. of water of crystallisation when dried at 125° until constant.

When the lactone of A-hydroxydimethylbutanetricarboxylic acid, (m. p. 158°) is heated at 200°, it is decomposed like the lactone of the B-acid with elimination of carbon dioxide and formation of a resinous substance very soluble in water. As it was thought at the time that this was probably the same acid (m. p. 108°) as that obtained from the lactone of the B-hydroxy-acid, the whole was boiled with excess of ammonia and calcium chloride, but no crystalline salt separated until the solution had been evaporated to a small bulk, and this on cooling and diluting with a little water again dissolved completely.

The whole was acidified and extracted with ether, and the residue, after distilling off the ether, allowed to stand over sulphuric acid, when it gradually became semi-solid. After 10 days, the mass was ground up in a mortar with concentrated hydrochloric acid, which dissolved the resinous impurity, and left a colourless, crystalline acid; this, after washing with hydrochloric acid, melted at 154—156°, with slight previous softening, and furnished the following numbers on analysis:

0·157 gave 0·3186 CO_2 and 0·0947 H_2O. C = 55·3; H = 6·7.

$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

The *lactone* of *A-hydroxydimethylbutanedicarboxylic acid* is much less soluble in water than that of the B-acid. That it is a monobasic lactonic acid is shown by the following results, which were obtained on titration with decinormal caustic soda.

0·145 gram dissolved in hot water and the solution, after cooling to 20°, titrated rapidly, neutralised 0·043 gram NaOH; on adding excess of decinormal caustic soda, boiling for a few minutes, and titrating back, it was found that 0·064 gram NaOH had been taken up. This amount of a monobasic acid, $C_8H_{12}O_4$, requires 0·034 gram NaOH, and if dibasic 0·067 gram NaOH, for neutralisation.

These numbers show, therefore, that the acid is a monobasic lactone acid, but, that in aqueous solution, partial hydrolysis of the lactone ring has taken place, such hydrolysis to the disbasic hydroxy-acid being complete when the solution is boiled with an excess of decinormal caustic soda.

Action of Sodium Ethoxide on Ethyl Dicarboxydimethyltrimethylenemalonate. Formation of the Yellow Sodium Compound of Ethyl Dimethylketodicyclopentanetricarboxylate,

$$Me_2C<\begin{matrix}C(CO_2Et)\cdot CNa\cdot CO_2Et\\ C(CO_2Et)\cdot CO\end{matrix}.$$

This interesting condensation was carried out in alcoholic solution with sodium ethoxide and also in xylene solution by the action of sodium, in both cases with the same result, so that the first experiment only need be described in detail.

The pure ethyl ester (5 grams) was dissolved in alcohol, mixed with an excess of a strong solution of sodium ethoxide containing 2 grams of sodium, and heated on the water-bath for 3 hours. The deep yellow solution was then evaporated to remove alcohol as far as possible, and mixed with water, when a quantity of the yellow sodium compound separated, and this, after washing first with water and then with alcohol and ether and drying at 100°, was analysed, with the following result:

0·3512 gave 0·0727 Na_2SO_4. Na = 6·7.

$C_{16}H_{21}O_7Na$ requires Na = 6·6 per cent.

This yellow sodium compound when dissolved in methyl alcohol gave an intense red coloration with ferric chloride, and on hydrolysis with dilute sulphuric acid was converted into *dimethylketodicyclopentanecarboxylic acid* melting at 180°; therefore there can be no doubt that it is identical with the yellow sodium compound which was subsequently prepared in large quantities by the process explained on p. 776.

On acidifying the mother liquor from which the sodium compound had been isolated as described above, an oil separated which, when hydrolysed with dilute sulphuric acid, gave a considerable quantity of the above ketonic acid melting at 180°. This oil, which is evidently an acid ethyl ester, is doubtless the same as that always produced in the preparation of the yellow sodium compound by the process given on p. 776.

Ethyl Dicarboxydimethyltrimethylenebromomalonate,

$$Me_2C<\begin{matrix}C(CO_2Et)\cdot CBr(CO_2Et)_2\\ CH\cdot CO_2Et\end{matrix},$$

When ethyl dicarboxydimethyltrimethylenemalonate (11 grams) was mixed with rather more than the theoretical quantity of bromine (5 grams) and the mixture heated on the water-bath in a flask fitted with a long air condenser, hydrogen bromide was evolved in quantity, and after 3 hours the whole of the bromine had disappeared. The product was poured into water, extracted with ether, the ethereal solution washed repeatedly with dilute sodium carbonate, dried over calcium chloride, and evaporated, when a heavy, brown oil was obtained which, after standing for some days over sulphuric acid in a vacuum, furnished the following results on analysis:

0·4342 gave 0·1863 AgBr. Br = 18·3.

$C_{18}H_{27}O_8Br$ requires Br = 17·7 per cent.

Hydrolysis with Alcoholic Potash.—When this bromo-ester was mixed with excess of alcoholic potash, hydrolysis took place readily, and after heating on the water-bath for 2 hours water was added, the clear liquid evaporated to dryness, acidified, and repeatedly extracted with ether.

The gum which remained after distilling off the ether was dissolved in a slight excess of ammonia and boiled with calcium chloride, by which means a considerable quantity of coloured impurity was precipitated.

After filtering, the filtrate was acidified, again extracted with ether, and the gummy acid heated at 200° until evolution of gas ceased; the dark coloured mass was then ground up with pure dry ether, which dissolved the oily impurity and left a small quantity of a sandy, crystalline powder. This was dissolved in much dry ether, the ethereal solution evaporated to a small bulk and allowed to stand, and the crystalline crust, which gradually separated, collected and analysed:

0·1214 gave 0·2425 CO_2 and 0·0554 H_2O. C = 54·5; H = 5·1.

$C_9H_{10}O_5$ requires C = 54·5; H = 5·1 per cent.

As explained in the introduction, it is exceedingly probable that this substance is

Anhydrodimethyltetramethylenetricarboxylic Acid,

$$Me_2C\begin{<}CH(CO_2H)\cdot CH\cdot CO\\ \quad\quad\quad\quad\quad\quad CH\cdot CO\end{>}O.$$

It melts at 207—210° and is very sparingly soluble in ether or light petroleum, but readily soluble in acetone; it dissolves readily in water on boiling, forming a very soluble acid, which, on evaporating the solution almost to dryness, is obtained in the form of crystals, but owing to the difficulty of purifying it, has not yet been isolated in a form suitable for analysis.

That a tribasic acid is formed in this way is proved by the following experiment. 0·0684 gram of the pure anhydro-acid was boiled with water and the solution titrated with decinormal sodium hydroxide, when 0·0416 gram NaOH were neutralised; assuming that the acid formed is tribasic, this amount should neutralise 0·0415 gram NaOH.

The solution thus obtained is stable to permanganate for several minutes, showing that the acid is saturated.

Ethyl Dicarboxydimethyltrimethylene-ethylmalonate,

$$Me_2C\begin{<}C(CO_2Et)\cdot CEt(CO_2Et)_2\\ CH\cdot CO_2Et\end{>}.$$

In preparing this ester, ethyl dicarboxydimethyltrimethylenemalonate (11 grams) was added to a solution of sodium (0·9 gram) in absolute alcohol (15 grams) and the yellow solution then mixed with ethyl iodide (10 grams) and heated for 6 hours on the water-bath. The oil, which was precipitated on adding water, was extracted with ether, the ethereal solution well washed with water, dried over calcium chloride, and evaporated, and the residual yellow oil fractionated, when almost the whole quantity passed over at 230—232° under 30 mm. pressure as a slightly yellow oil, which was analysed with the following results:

0·1633 gave 0·3516 CO_2 and 0·1141 H_2O. C = 58·7; H = 7·7.
$C_{20}H_{32}O_8$ requires C = 60·0; H = 8·0 per cent.

As the results of analysis seemed to indicate that the substance might still contain some of the original ester, which had escaped the action of the sodium ethoxide and ethyl iodide, it was treated again, exactly as before, with these reagents. The product, which distilled at the same temperature as before, now furnished correct results on analysis:

0·1754 gave 0·3871 CO_2 and 0·1239 H_2O. C = 60·2; H = 7·8.
0·1403 ,, 0·3088 CO_2 ,, 0·1019 H_2O. C = 60·0; H = 8·1.
$C_{20}H_{32}O_8$ requires C = 60·0; H = 8·0 per cent.

Ethyl dicarboxydimethyltrimethylene-ethylmalonate, which is formed almost quantitatively in the above reaction, is a thick oil which, when heated in small quantities, appears to distil under the ordinary pressure, almost without decomposition.

Dimethylethylethoxyketopentamethylenedicarboxylic Acid,



This substance is produced by the hydrolysis of the ester described in the previous section. The pure ester (20 grams) was added to a solution of potash (25 grams) in methyl alcohol, when a dark yellow solution was produced which, on boiling, gradually became dark brown. After 2 hours water was added, the solution evaporated until free from alcohol, extracted with ether to remove a trace of neutral oil, acidified, and the liquid, after saturating with ammonium sulphate, extracted 20 times with ether; the ethereal solution was then dried over calcium chloride and evaporated. The dark-brown residue (12 grams) gradually deposited crystals, and after 10 days the semi-solid mass was well stirred with a little cold water, filtered on the pump, and the ochre-coloured residue (6 grams) dissolved in hot water, boiled with animal charcoal, and filtered. The filtrate on slowly cooling deposited beautiful, glistening, prismatic needles, which were collected, recrystallised from water, and analysed:

0·178 gave 0·3736 CO_2 and 0·1197 H_2O. C = 57·2; H = 7·5.
$C_{13}H_{20}O_6$ requires C = 57·3; H = 7·3 per cent.

The acid melts at 175° without decomposition, but gives off gas slowly at 190°, much more rapidly at 200—210°.

The *silver* salt, $C_{13}H_{18}O_6Ag_2$, was obtained as a white, crystalline powder on adding silver nitrate to a warm, slightly alkaline solution of the ammonium salt. On analysis:

0·2165 gave 0·2520 CO_2, 0·075 H_2O, and 0·0954 Ag.
C = 31·7; H = 3·8; Ag = 44·1.
$C_{13}H_{18}O_7Ag_2$ requires C = 32·1; H = 3·7; Ag = 44·3 per cent.

As this substance was at first thought to be an acid ester (see p. 748), experiments were tried as to its behaviour with strong alkalis, with the view of further hydrolysing it.

It was found, however, that digestion with aqueous potash or baryta apparently had no effect on it, as, on acidifying, the greater part of the substance was recovered unchanged. In one experiment, the substance was digested with a large excess of aqueous potash (10 per cent.) for 2 hours when, on acidifying and extracting with ether, a

solid was obtained which crystallised beautifully from water, and furnished the following numbers on analysis:

0·1628 gave 0·3462 CO_2 and 0·1071 H_2O. C = 57·9; H = 7·3.

$C_{13}H_{20}O_6$ requires C = 57·3; H = 7·3 per cent.

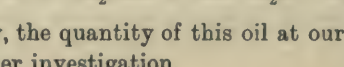
Since these crystals melted at 170—175°, it is evident that boiling with potash had not effected any change in the substance.

When the pure substance is heated in a fractionating flask, it decomposes and gives off a small quantity of a liquid of low boiling point which is apparently alcohol; the residue then distils at 270—300° with hardly any charring. On redistillation, almost the whole quantity passed over at 270—275° as a colourless oil which, on analysis, gave the following numbers:

0·1524 gave 0·3614 CO_2 and 0·1031 H_2O. C = 64·7; H = 7·5.

Unfortunately, the quantity of this oil at our disposal was too small to allow of further investigation.

Lactone of Dimethylethylhydroxybutanetetracarboxylic Acid,



The dark-coloured aqueous mother liquors obtained after the separation of the crystals of dimethylethylethoxyketopentamethylenedicarboxylic acid from the semi-solid product of the hydrolysis of ethyl dicarboxydimethyltrimethylene-ethylmalonate, as described in the last section, were boiled with an excess of barium hydroxide, and the almost colourless, bulky, amorphous precipitate which formed was collected on the pump and well washed with water.

The salt was then decomposed by dilute hydrochloric acid, the clear solution extracted 10 times with ether, the ethereal solution dried over calcium chloride and evaporated, when a transparent, resinous residue was obtained, which on rubbing with a glass rod gradually became semi-solid. The mass was left in contact with porous porcelain until dry, and purified by recrystallisation from warm water with the aid of animal charcoal. The substance separates from water in minute prisms, and under the microscope is seen to be quite homogeneous; it melts at about 193°, with evolution of gas.

0·178 gave 0·3275 CO_2 and 0·0906 H_2O. C = 50·1; H = 5·6.

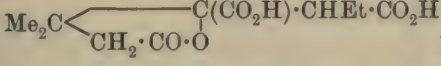
$C_{12}H_{16}O_8$ requires C = 50·0; H = 5·6 per cent.

That this substance is the *lactone* of *dimethylethylhydroxybutanetetracarboxylic acid*, and has the constitution represented at the head of this section, is rendered probable, not only by the analysis, but also by the results obtained on titration with decinormal sodium hydroxide.

0·2075 gram dissolved in cold water and rapidly titrated, required for neutralisation 0·084 gram NaOH, whereas this amount of a substance of the formula $C_{12}H_{16}O_8$, if *tribasic*, should neutralise 0·086 NaOH. On boiling with an excess of the alkali for a few minutes and titrating back, it was found that 0·115 gram of NaOH had now been neutralised, indicating that hydrolysis of a lactone ring had taken place, and the substance become *tetrabasic;* this would require 0·115 gram NaOH.

It would be interesting to ascertain what compound is formed when this substance decomposes at 193°, but unfortunately the small quantity of material at our disposal was insufficient for the purpose.

Lactone of trans-*Dimethylethylhydroxybutanetricarboxylic Acid*,



The dark brown aqueous filtrate from the insoluble barium salt described in the last section was acidified and repeatedly extracted with ether, when, on evaporation of the ether, a new acid was obtained which crystallised well from water in prismatic needles, and melted at about 213° without decomposition. This was analysed, with the following results:

0·1548 gave 0·3027 CO_2 and 0·0890 H_2O. C = 53·3; H = 6·4.

$C_{11}H_{16}O_6$ requires C = 54·1; H = 6·5 per cent.

During the combustion, it was noticed that a beautifully crystalline sublimate, probably of an anhydride, formed on the cooler portions of the tube. Although this substance has only been obtained in small quantities, it is probable that it is one of the stereoisomeric modifications of the *lactone* of *dimethylethylhydroxybutanetricarboxylic acid*, and as it melts at a higher temperature than the other modification (see next section) and is not, like the latter, converted into an anhydride at this temperature, we have named it the *trans*-modification.

That this substance is a dibasic lactonic acid is borne out by the results of the following titration with decinormal sodium hydroxide, which was carried out with the remaining small quantity of the material.

0·0522 gram required for neutralisation 0·0165 gram NaOH, whereas, if *dibasic*, it should have neutralised 0·0171 gram NaOH. On boiling with excess of alkali and titrating back, it was found that 0·024 gram NaOH had been neutralised, indicating that a lactone ring had been hydrolysed and the acid become *tribasic*; this would require 0·0256 gram NaOH.

Lactone of cis-*Dimethylethylhydroxybutanetricarboxylic Acid.*

This acid has been prepared in considerable quantity by the hydrolysis of dimethylethylethoxyketopentamethylenedicarboxylic acid with hydrochloric acid. The pure substance was boiled with concentrated hydrochloric acid in a reflux apparatus until the crystals had completely dissolved, which was the case after about six hours. On standing overnight, a small quantity of colourless, needle-shaped crystals had formed, and a further large quantity separated on vigorously shaking the liquid; these were collected and purified by crystallisation from water.

This new substance exhibits in a marked degree the tendency to form supersaturated solutions; when it crystallises moderately rapidly it is obtained in the form of needles, but when the separation is slow and extends over several days, it is deposited in hard prisms, somewhat resembling crystals of cane sugar.

These prisms gave the following results on analysis, showing that in this form the substance crystallises with water:

0·1522 gave 0·281 CO_2 and 0·0959 H_2O. C = 50·4; H = 7·0.
$C_{11}H_{16}O_6,H_2O$ requires C = 50·4; H = 6·9 per cent.

On the other hand, a specimen from a different preparation which had separated from hydrochloric acid in flat, glistening needles was evidently anhydrous.

0·14 gave 0·276 CO_2 and 0·0851 H_2O. C = 53·7; H = 6·7.
$C_{11}H_{16}O_6$ requires C = 54·1; H = 6·5 per cent.

The *lactone* of cis-*dimethylethylhydroxybutanetricarboxylic acid* has no definite melting point, since when heated in a capillary tube it decomposes, with evolution of gas, at temperatures ranging from about 144° in the case of the prisms to 153° in the case of the needles. It dissolves much more readily in water than the ethoxy-acid from which it was obtained, and on titration with decinormal sodium hydroxide it gives numbers which characterise it as a dibasic lactonic acid.

0·4478 gram of the prisms, dissolved in cold water, neutralised 0·147 gram NaOH, whereas this quantity of a *dibasic acid* of the formula $C_{11}H_{16}O_6,H_2O$ should neutralise 0·133 gram NaOH. This shows that on dissolving the substance in water partial hydrolysis of the lactone ring takes place. Excess of decinormal sodium hydroxide was now added, and after the liquid had been boiled for some time it was found, on titrating back, that 0·196 gram NaOH had been neutralised, whereas for the neutralisation of the *tribasic acid*, 0·192 gram should have been taken up.

Silver Salt, $C_{11}H_{15}O_7Ag_3$.—In preparing this salt, the acid was boiled with water and excess of ammonia, evaporated until nearly neutral, and precipitated with silver nitrate. The white, amorphous salt thus obtained gave numbers, on analysis, showing that it was the salt of the tribasic acid and not of the dibasic lactonic acid.

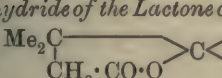
0·2412 gave 0·1317 Ag. Ag = 54·6.

$C_{11}H_{15}O_7Ag_3$ requires Ag = 55·1 per cent.

The tribasic *barium* salt, $(C_{11}H_{15}O_7)_2Ba_3$, is obtained on adding excess of boiling barium hydroxide solution to a hot aqueous solution of the lactonic acid, as a heavy, white precipitate, which was rapidly collected on the pump, washed with boiling water, dried at 100°, and analysed :

0·5421 gave 0·4083 $BaSO_4$. Ba = 44·3.

$C_{22}H_{30}O_{14}Ba_3$ requires Ba = 44·2 per cent.

Anhydride of the Lactone of cis-*Dimethylethylhydroxybutanetricarboxylic Acid*,  —If the acid is heated at 180° until the evolution of gas has ceased, and then allowed to solidify, its melting point will now be found to be 160—164°, a change which is due to the formation of the anhydride. This anhydride is easily obtained in a pure condition when the acid is heated for half an hour with excess of acetyl chloride and the solution evaporated to dryness. The solid residue is powdered, extracted with boiling light petroleum (b. p. 80—100°), which removes a trace of impurity but dissolves very little of the anhydride, and the residue is crystallised from benzene, from which it separates in lustrous plates. On analysis :

0·1701 gave 0·3638 CO_2 and 0·0981 H_2O. C = 58·3 ; H = 6·4.

$C_{11}H_{14}O_5$ requires C = 58·4 ; H = 6·2 per cent.

This anhydride melts at 168° and solidifies rapidly again at a few degrees below this temperature ; it is slowly hydrolysed by boiling water, and the solution, on evaporation over sulphuric acid, deposits colourless crystals decomposing at 144° and consisting of the original dibasic lactonic acid, no stereoisomeric change having taken place during the formation of the anhydride.

Experimental.

Part II. Preparation and Properties of the Yellow Sodium Compound of Ethyl 5:5-*Dimethyl*-3-*ketodi*cyclo*pentane*-1:2:4-*tricarboxylate and Description of the Acids obtained from it.*

By W. H. Perkin, jun., J. F. Thorpe, and C. Walker.

Condensation of Ethyl $\alpha\alpha_1$-*Dibromo*-$\beta\beta$-*dimethylglutarate with Ethyl Malonate in the Presence of Excess of Sodium Ethoxide. Preparation of the Sodium Compound of Ethyl Dimethylketodi*cyclo*pentane-tricarboxylate*, $Me_2C<\begin{matrix}C(CO_2Et)\cdot CNa\cdot CO_2Et\\ |\\ C(CO_2Et)\cdot CO\end{matrix}$.

This sodium compound, the formation of which by the action of sodium on ethyl dicarboxydimethyltrimethylenemalonate has been mentioned on p. 768, is best prepared in quantity by the following process.

Ethyl malonate (2 mols.) is mixed with a solution of sodium (4 at). dissolved in alcohol, and then ethyl dibromodimethylglutarate (1 mol.) is gradually added. The mass at once assumes a deep yellow colour, which intensifies on heating on the water-bath, and if, after heating for 12 hours, the alcohol is distilled off and water added, a large yield of a yellow solid is precipitated; this can be separated by filtration and washed with water without undergoing change. The method usually adopted was to filter off the yellow sodium compound through a Buchner funnel on the pump, wash twice with water, then once with alcohol, and finally with dry ether, until all trace of oil had been removed.

For analysis, the yellow sodium compound was crystallised from boiling alcohol, from which it separates, on cooling, in lustrous yellow plates.

0·1790 gave 0·0370 Na_2SO_4. Na = 6·69.

$C_{16}H_{21}O_7Na$ requires Na = 6·60 per cent.

The yellow sodium compound prepared in this way is identical with that obtained by the method given on p. 768, where the principal properties of the substance are mentioned. The yield obtained by the above process is 60—65 per cent. of the theoretical.

From the ethereal and alcoholic washings of the sodium compound, a neutral and an acid portion can be extracted by shaking with sodium carbonate solution.

The neutral portion consists for the most part of unchanged ethyl malonate mixed with a small quantity of ethyl ethanetetracarboxylate, $(CO_2Et)_2CH\cdot CH(CO_2Et)_2$, melting at 76°.

The sodium carbonate solution, on acidifying, deposits a thick oil, which gives an intense red coloration with ferric chloride, and on hydrolysis with dilute sulphuric acid is converted into *dimethylketodicyclopentanecarboxylic acid* (p. 780).

Action of Cold Methyl Alcoholic Potash on the Yellow Sodium Compound. Formation of Diethyl Hydrogen Dimethylketodicyclopentanetricarboxylate and its Dipotassium Salt,

$$Me_2C<\begin{matrix}C(CO_2Et)\cdot CH\cdot CO_2Et\\ C(CO_2H)-CO\end{matrix} \quad \text{and} \quad Me_2C<\begin{matrix}C(CO_2Et)\cdot CK\cdot CO_2Et\\ C(CO_2K)-CO\end{matrix}.$$

When the yellow sodium compound is treated in the cold with an equal weight of potash dissolved in methyl alcohol, it passes into solution, and in a short time a large quantity of a *canary-yellow* potassium salt separates. This was collected on the pump, washed with methyl alcohol, and analysed, with the following result:

0·4878 gave 0·2066 K_2SO_4. K = 21·5.
$C_{14}H_{16}O_7K_2$ requires K = 21·0 per cent.

This potassium salt, which evidently has the constitutional formula represented above, is fairly soluble in cold water, and on acidifying the solution an oil is precipitated, which gradually sets to a solid mass of the corresponding diethyl hydrogen salt, a colourless substance which separates from dilute alcohol in long prisms and melts at 75°. On analysis:

0·1777 gave 0·3680 CO_2 and 0·0975 H_2O. C = 56·5; H = 6·1.
$C_{14}H_{18}O_7$ requires C = 56·4; H = 6·0 per cent.

This substance is very sparingly soluble in water, but readily so in sodium carbonate. Its alcoholic solution gives an intense purple coloration with ferric chloride.

B-Dimethylketodicyclopentanedicarboxylic Acid,

$$Me_2C<\begin{matrix}C(CO_2H)\cdot CH\cdot CO_2H\\ CH\text{———}CO\end{matrix}.$$

When the diethyl hydrogen salt, described in the last section, is heated under 30 mm. pressure, carbon dioxide is eliminated, and a thick oil distils over constantly at 210°, which gives in alcoholic solution, on the addition of ferric chloride, a rich purple coloration, and, as the analysis shows, consists of *ethyl dimethylketodicyclopentanedicarboxylate.*

0·2341 gave 0·5252 CO_2 and 0·1477 H_2O. C = 61·2; H = 7·0.
$C_{13}H_{18}O_5$ requires C = 61·4; H = 7·1 per cent.

On hydrolysing this ester with an equal weight of potash dissolved in alcohol, evaporating off the alcohol, acidifying with hydrochloric acid, and repeatedly extracting with ether, the corresponding acid is obtained as a solid, which crystallises from hydrochloric acid in long needles melting at 180°.

0·1568 gave 0·3073 CO_2 and 0·0750 H_2O. C = 53·6 ; H = 5·3.
0·1773 ,, 0·3530 CO_2 ,, 0·0813 H_2O. C = 54·3 ; H = 5·1.
$C_9H_{10}O_5$ requires C = 54·5 ; H = 5·1 per cent.

*B-Dimethylketodi*cyclo*pentanedicarboxylic acid* is very readily soluble in water, but much less so in hydrochloric acid ; its aqueous solution gives, with ferric chloride, a red coloration, and its solution in sodium carbonate is stable to permanganate for about 10 seconds.

The *silver* salt, $C_9H_8O_5Ag_2$, separates from a neutral solution of the ammonium salt, on the addition of silver nitrate, as a white, amorphous precipitate.

0·3145 gave 0·1642 Ag. Ag = 52·2.
$C_9H_8O_5Ag_2$ requires Ag = 52·3 per cent.

The *anhydride*, $C_9H_8O_3$, was prepared by boiling 2 grams of the acid with excess of acetic anhydride for 3 hours on the sand-bath, and then allowing the solution to evaporate over potash in a vacuous desiccator. The solid residue, which melted at about 150°, was dissolved in boiling light petroleum (b. p. 60—80°), filtered, and allowed to stand, when lustrous needles of the anhydride separated.

0·2134 gave 0·5134 CO_2 and 0·0928 H_2O. C = 65·6 ; H = 4·8.
$C_9H_8O_3$ requires C = 65·8 ; H = 4·8 per cent.

This substance melts at 152°, and is gradually dissolved by boiling water, being converted into the acid melting at 180°, from which it was derived.

On heating an aqueous solution of the acid at 180° for 6 hours, it was found to have been transformed into an acid sparingly soluble in water, and at the same time a considerable pressure was noticed on opening the tube. The acid thus produced crystallised from water in fern-like needles, melted at 180°, and was found to be identical with *dimethylketodi*cyclo*pentanecarboxylic acid* (p. 780) prepared by the action of dilute sulphuric acid on the sodium compound, and also by the action of heat on the A-modification of dimethylketodi*cyclo*pentane-dicarboxylic acid (p. 779).

Action of Boiling Alcoholic Potash on the Yellow Sodium Compound. Formation of A- and B-Dimethylketodicyclopentanedicarboxylic Acids,

$$Me_2C<\begin{matrix}C(CO_2H)\cdot CH\cdot CO_2H\\ |\qquad\qquad |\\ CH\text{——}CO\end{matrix}.$$

When the yellow sodium compound (20 grams) is boiled with potash (16 grams) dissolved in alcohol, a copious precipitate of a *colourless* potassium salt separates from the clear solution after the heating has been continued for 2 hours. This potassium salt, which is very deliquescent, is rapidly collected on the pump, washed with absolute alcohol, dissolved in a little water, acidified, and repeatedly extracted with ether; the ethereal solution is then dried and evaporated, when a solid acid is obtained, which melts indefinitely between 140° and 170°. This solid is a mixture of the A- and B-modifications of dimethylketodi*cyclo*pentanedicarboxylic acid, and can be resolved into these by dissolving it in a small quantity of water and adding an equal volume of concentrated hydrochloric acid. On allowing the solution to stand, a crystalline acid slowly separates, consisting of the almost pure A-modification.

This acid is less soluble in water than the B-modification, and separates from dilute hydrochloric acid (1 : 1) in small prisms which melt at 153—155°, and undergo decomposition with evolution of carbon dioxide at 165°; its aqueous solution gives, with ferric chloride, an intense bluish-violet coloration.

0·1493 gave 0·2911 CO_2 and 0·0719 H_2O. C = 53·1; H = 5·3.
0·1738 ,, 0·3388 CO_2 ,, 0·0814 H_2O. C = 53·2; H = 5·2.
$C_9H_{10}O_5$ requires C = 54·5; H = 5·1 per cent.

These numbers are not so good as could have been wished, and this is apparently due to the acid containing a small quantity of the tribasic acid, directly derived from the yellow sodium compound.

That the acid has the constitution given to it at the head of this section is proved by the fact that when heated above its melting point, or boiled with dilute sulphuric acid, it is converted with loss of carbon dioxide into *dimethylketodicyclopentanecarboxylic acid* melting at 180° (p. 780).

In this respect, it differs in a marked manner from the B-modification, which remains unaltered even after prolonged boiling with dilute sulphuric acid.

On evaporating the hydrochloric acid mother liquors of the A-acid, a considerable quantity of the B-modification (p. 778) is readily obtained, the proportion of each produced in the experiment described being about 1 of A to 3 of B. The proportion in which these acids are formed, however, depends entirely upon the length of time the mixture is

heated during the process of hydrolysis; should the heating be continued longer than 2 hours, then the A-modification is rapidly decomposed, with formation of the monocarboxylic acid melting at 180° (see next section).

*Action of Dilute Sulphuric Acid on the Yellow Sodium Compound. Formation of Dimethylketodi*cyclo*pentanecarboxylic Acid,*

$$Me_2C<\begin{matrix}C(CO_2H)\cdot CH_2\\ |\quad\quad |\\ CH\text{——}CO\end{matrix}.$$

In carrying out this decomposition, 10 grams of the yellow sodium compound were boiled for 6 hours with a 25 per cent. solution of sulphuric acid, when, on allowing the product to cool, a large quantity of a crystalline acid separated. This was collected, recrystallised from water, and analysed:

0·1960 gave 0·4481 CO_2 and 0·1163 H_2O. C = 62·3; H = 6·6.
$C_8H_{10}O_3$ requires C = 62·3; H = 6·6 per cent.

*Dimethylketodi*cyclo*pentanecarboxylic acid* separates from water, in which it is sparingly soluble, in fern-like needles, and melts at 180°; when carefully heated, it sublimes in long, silky needles. It is moderately soluble in hot benzene, and crystallises out on cooling in small plates. The aqueous solution of the acid gives no coloration with ferric chloride; but if the crystals of the acid are moistened with fuming nitric acid, a deep red solution is produced.

The *silver* salt, $C_8H_9O_3Ag$, separates from a neutral solution of the ammonium salt on the addition of silver nitrate, as a white, crystalline precipitate, which dissolves in much boiling water, and crystallises out, on cooling, in long needles.

0·1101 gave 0·1492 CO_2, 0·0369 H_2O, and 0·0450 Ag.
= 36·9; H = 3·7; Ag = 41·0.
$C_8H_9O_3Ag$ requires C = 36·8; H = 3·5; Ag = 41·3 per cent.

The *semicarbazone*, $C_7H_{10}O_2\cdot C{:}N_2H\cdot CO\cdot NH_2$, separates as an insoluble, sandy precipitate when a mixture of the acid, sodium acetate, and semicarbazide hydrochloride, dissolved in water, is boiled for a few minutes. It crystallises from dilute acetic acid in long, silky needles, which decompose at 255°.

0·1412 gave 25 c.c. nitrogen at 15° and 750 mm. N = 20·4.
$C_9H_{13}O_3N_3$ requires N = 20·0 per cent.

The *hydrazone*, $C_7H_{10}O_2\cdot C{:}N_2H\cdot C_6H_5$, is formed when a solution of phenylhydrazine in glacial acetic acid is added to an aqueous solution of the acid and the mixture boiled for a short time. It separates from dilute acetic acid in yellow needles, which decompose at 217°.

0·1849 gave 19 c.c. nitrogen at 16° and 767 mm. N = 12·2.
$C_{14}H_{16}O_2N_2$ requires N = 11·4 per cent.

This hydrazone is very sparingly soluble in water, but dissolves readily in sodium carbonate solution.

The yield of dimethylketodi*cyclo*pentanecarboxylic acid, obtained from the yellow sodium compound in the way described above, is about 30 per cent. of the theoretical, and the aqueous liquors from which it has crystallised give, on extraction with ether and evaporating, a crystalline residue, which consists entirely of the B-modification of dimethylketodi*cyclo*pentanedicarboxylic acid (p. 778). In preparing the monocarboxylic acid, it was found most convenient to extract the product of hydrolysis of the yellow sodium compound (see above) with ether, and after evaporating off the ether, to heat the residue with water in sealed tubes at 180° for 5 hours, when the B-modification of the dibasic acid is also completely converted into the monobasic acid. It is evident, therefore, that only the A-modification of the dibasic acid is converted into the monobasic acid during the hydrolysis of the yellow sodium compound with sulphuric acid, the B-modification remaining unchanged. It has previously been mentioned (p. 779) that the B-modification is stable to dilute sulphuric acid.

*Oxidation of Dimethylketodi*cyclo*pentanecarboxylic Acid. Formation of αα-Dihydroxy-ββ-dimethylglutaric Acid,*
$CO_2H{\cdot}C(OH)_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$,
and of αα-Dimethylsuccinic Acid, $CO_2H{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$.

The solution of the ketonic acid in sodium carbonate is only very slowly oxidised by potassium permanganate at the ordinary temperature, and it was found necessary, in order to facilitate oxidation, to heat the mixture at about 80—90°. About 12 grams of the acid dissolved in sodium carbonate were mixed with a small quantity of permanganate and heated on the water-bath for twelve hours, further quantities of permanganate being added from time to time as soon as the pink colour became discharged. The excess was then removed by sulphur dioxide, and the solution, after filtering, evaporated to a small bulk, acidified, and extracted with ether. The solid residue obtained on evaporating the ethereal solution was then recrystallised from chloroform, from which it separated in prismatic, apparently homogeneous, needles melting between 84° and 90°.

0·1774 gave 0·3026 CO_2 and 0·0982 H_2O. C = 46·5 ; H = 6·1.
$C_7H_{12}O_6$ requires C = 43·8 ; H = 6·2 per cent.

For a long time we were unable to discover the nature of this substance, but ultimately it was shown to consist of a mixture of αα-di-

hydroxydimethylglutaric acid and *aa*-dimethylsuccinic acid. These acids are exceedingly difficult to separate by crystallisation, but the separation was eventually effected by taking advantage of the difference in the properties of their calcium salts. The mixed acids were dissolved in water, excess of ammonia and calcium chloride was added, and the mixture allowed to stand, when a crystalline, very sparingly soluble salt gradually began to separate, the separation being complete in 12 hours.

The calcium salt was collected, washed, dried at 100°, and by analysis and isolation of the acid proved to be the calcium salt of *aa*-dihydroxydimethylglutaric acid.

0·3150 gave 0·1858 $CaSO_4$. Ca = 17·1.
$C_7H_{10}O_6Ca$ requires Ca = 17·3 per cent.

To obtain the acid, the calcium salt was suspended in cold water and acidified with excess of hydrochloric acid, ammonium sulphate was then added, and the solution repeatedly extracted with ether. The solid extract separated from chloroform in needles melting at 84°, and proved to be *aa-dihydroxydimethylglutaric acid* (see p. 757).

0·1706 gave 0·2761 CO_2 and 0·1006 H_2O. C = 44·1 ; H = 6·5.
0·1448 „ 0·2322 CO_2 „ 0·0851 H_2O. C = 43·7 ; H = 6·5.
$C_7H_{12}O_6$ requires C = 43·8 ; H = 6·2 per cent.

The filtrate from the calcium salt of this acid, on boiling, deposited a further small quantity of a calcium salt. This was collected, decomposed with hydrochloric acid, and extracted with ether. The solid residue which was obtained on evaporating off the ether crystallised from water, in which it was exceedingly soluble, in small prisms melting at 137—138°.

0·1791 gave 0·3233 CO_2 and 0·1101 H_2O. C = 49·2 ; H = 6·8.
$C_6H_{10}O_4$ requires C = 49·3 ; H = 6·8 per cent.

A careful examination of this acid proved it to be *aa-dimethylsuccinic acid.* By far the larger proportion of the acids produced in this oxidation consists of *aa*-dihydroxydimethylsuccinic acid, since from the 12 grams used in the experiment only enough dimethylsuccinic acid was obtained for analysis and identification.

Reduction of Dimethylketodicyclopentanecarboxylic Acid. Formation of Dimethylketopentamethylenecarboxylic Acid,

$$Me_2C\begin{matrix}<\text{CH}(CO_2H)\cdot\text{CH}_2\\ \text{CH}_2\text{———CO}\end{matrix}.$$

This acid is obtained when a solution of dimethylketodicyclopentanecarboxylic acid (7 grams) in dilute sodium carbonate is allowed

to remain in contact with 3 per cent. sodium amalgam (300 grams) in a flat porcelain dish for 12 hours with frequent stirring, a current of carbon dioxide being led through the liquid during the whole operation.

The solution, after filtering and acidifying, was saturated with ammonium sulphate and extracted several times with ether. The ethereal solution was then evaporated, when a solid acid was obtained which crystallised from water in small prisms.

0·1729 gave 0·3898 CO_2 and 0·1221 H_2O. C = 61·5; H = 7·8.
$C_8H_{12}O_3$ requires C = 61·5; H = 7·7 per cent.

Dimethylketopentamethylenecarboxylic acid melts at 103°, and is readily soluble in water. When heated in small quantities, it distils unchanged.

The *oxime*, $C_7H_{12}O_2C{:}N{\cdot}OH$, was prepared by dissolving the acid in dilute sodium carbonate and adding an excess of hydroxylamine hydrochloride. After standing for 2 days, the solution was acidified, saturated with ammonium sulphate, and extracted at least 20 times with ether, since the substance is only extracted with difficulty from its aqueous solution by this solvent. The ethereal solution, after drying over calcium chloride and evaporating to a small bulk, deposited the oxime in the form of crystalline crusts, which are very sparingly soluble in ether, and melt at 188—190° with decomposition.

0·1708 gave 12·6 c.c. nitrogen at 17° and 746 mm. N = 8·4.
$C_8H_{13}O_3N$ requires N = 8·2 per cent.

The *semicarbazone*, $C_7H_{12}O_2C{:}N_2H{\cdot}CO{\cdot}NH_2$, separates on boiling the acid with a solution of semicarbazide hydrochloride and sodium acetate as a white, sandy precipitate which crystallises from a large volume of hot water in small needles and decomposes at 215°.

0·2077 gave 35·2 c.c. nitrogen at 19·5° and 760 mm. N = 19·4.
$C_9H_{15}O_3N_3$ requires N = 19·7 per cent.

Dimethylhydroxypentamethylenecarboxylic acid,

$$Me_2C\begin{cases}CH(CO_2H){\cdot}CH_2\\ CH_2\text{———}CH{\cdot}OH\end{cases}$$

This acid is formed when dimethylketodi*cyclo*pentanecarboxylic acid is treated with a large excess of sodium amalgam, and is obviously produced by the reduction of the ketonic acid described in the last section.

In preparing it, 7 grams of dimethylketodi*cyclo*pentanecarboxylic acid, dissolved in sodium carbonate, are left in contact with at least 600 grams of 3 per cent. sodium amalgam for 24 hours; the product

is then acidified, extracted repeatedly with ether, and the ethereal extract, after drying over calcium chloride, evaporated.

The crystalline residue dissolves readily in hot water, and on cooling, a small quantity of dimethylketopentamethylenecarboxylic acid separates first. This is removed by filtration, the filtrate rendered alkaline with ammonia, excess of calcium chloride added, and the solution boiled, when a large quantity of a sparingly soluble calcium salt is gradually deposited.

The salt is collected, washed with water, decomposed with hydrochloric acid, and the solution, after saturating with ammonium sulphate, extracted repeatedly with ether. On evaporating off the ether and crystallising the residue from benzene, the pure hydroxy-acid is obtained in the form of small needles.

0·1845 gave 0·3898 CO_2 and 0·1488 H_2O. C = 60·6 ; H = 8·9.
$C_8H_{14}O_3$ requires C = 60·8 ; H = 8·8 per cent.

Dimethylhydroxypentamethylenecarboxylic acid melts at 115° and is very soluble in water. It dissolves readily in hot benzene, but is rather sparingly soluble in this solvent in the cold.

Action of Sulphuric Acid.—When the hydroxy-acid is mixed with a large excess of sulphuric acid, a slight rise of temperature takes place, and, at the same time, large quantities of sulphur dioxide are evolved. The evolution of gas ceases after 3 hours if the mixture is left at the ordinary temperature, and on pouring the product into cold water, a curious green solid separates. When thoroughly washed with boiling water and dried, this substance is an olive-green, amorphous powder which gradually becomes yellow on exposure to the air. This green substance is evidently of very high molecular weight, since it melts above 300° ; it dissolves in sodium carbonate, forming a reddish-brown solution, from which the original green compound is precipitated on acidifying. It dissolves in glacial acetic acid, forming an intense indigo-blue solution, the colour of which, on standing, gradually changes to a dark brown.

The filtrate from the calcium salt of the hydroxy-acid (see above) was acidified, evaporated to dryness, and extracted with ether, when a substance was obtained which separated from dilute acetone as a microcrystalline powder. On analysis :

0·1865 gave 0·4438 CO_2 and 0·1272 H_2O. C = 65·1 ; H = 7·6.
$C_{16}H_{22}O_5$ requires C = 65·3 ; H = 7·5 per cent.

This substance, which melts at 205° with partial sublimation, most probably has the constitution represented by the formula,

$$Me_2C\begin{array}{l}\diagup CH(CO_2H)\cdot C=C\cdot CH_2\diagdown\\ \diagdown CH_2\text{———}CO\quad CH_2\cdot CH(CO_2H)\diagup\end{array}CMe_2,$$

that is to say, it is produced by the condensation of 2 mols. of dimethylketopentamethylenecarboxylic acid by the alkali formed during the reduction. It has been found that this substance is only produced if the reduction described above is conducted without neutralising the caustic soda formed; if a rapid stream of carbon dioxide is passed during the reduction, no trace of the substance melting at 205° appears to be formed.

Oxidation of Dimethylketopentamethylenecarboxylic Acid. Formation of aa-Dimethylsuccinic Acid, $CO_2H\cdot CMe_2\cdot CH_2\cdot CO_2H$, *and ββ-Dimethylglutaric Acid,* $CO_2H\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CO_2H$.

I. *Oxidation with strong Nitric Acid.*—The ketonic acid (3 grams) was dissolved in strong nitric acid, and heated on the water-bath until the evolution of red fumes had ceased. On evaporating repeatedly to dryness with water, a solid residue was obtained which separated from dilute hydrochloric acid in small prisms and melted at 137—138°.

0·2150 gave 0·3887 CO_2 and 0·1298 H_2O. C = 49·3; H = 6·7.
$C_6H_{10}O_4$ requires C = 49·3; H = 6·8 per cent.

That this acid was *aa-dimethylsuccinic acid* was shown by dissolving it in excess of ammonia, adding calcium chloride, and boiling, when the characteristic calcium salt separated at once.

The remainder of the acid was digested with acetyl chloride and evaporated, when the anhydride of dimethylsuccinic acid was obtained in crystals melting at 29°.

II. *Oxidation with dilute Nitric Acid.*—The ketonic acid (3 grams) was heated with dilute nitric acid (sp. gr. 1·2) on the water-bath until the evolution of red fumes had ceased. The solution was then evaporated to dryness and the solid residue recrystallised three times from dilute hydrochloric acid. The crystals thus obtained were further recrystallised from ether and then analysed:

0·3141 gave 0·6025 CO_2 and 0·2092 H_2O. C = 52·3; H = 7·4.
$C_7H_{12}O_4$ requires C = 52·5; H = 7·5 per cent.

This acid melted at 101—102°, and on treatment with acetic anhydride yielded an anhydride melting at 123°; it therefore consisted of *ββ-dimethylglutaric acid,* $CO_2H\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CO_2H$ (Perkin and Goodwin, Trans., 1896, 69, 1474).

Action of Methyl Iodide on the Yellow Sodium Compound. Formation of Ethyl Trimethylketodicyclopentanetricarboxylate,

$$Me_2C<\begin{matrix}C(CO_2Et)\cdot CMe\cdot CO_2Et\\ C(CO_2Et)\cdot CO\end{matrix}.$$

In order to prepare this compound, 25 grams of the pure yellow sodium compound were dissolved in 75 grams of boiling ethyl alcohol, three times the theoretical quantity of methyl iodide (26 grams) were added, and the mixture was heated on the water-bath for 24 hours, at the end of which time it was found that the original deep yellow colour of the solution had entirely disappeared. After distilling off the alcohol and unchanged methyl iodide, the oil which separated on the addition of water was extracted with ether, and the ethereal solution shaken repeatedly with dilute sodium carbonate to remove some substance which dissolves with a yellow colour.

The ethereal solution was then dried over calcium chloride, the ether distilled off, and the residual oil fractionated under 20 mm. pressure, when almost the whole quantity distilled at 219° as a colourless oil.

I. 0·1873 gave 0·4101 CO_2 and 0·1205 H_2O. C = 59·7; H = 7·1.
II. 0·1979 „ 0·4347 CO_2 „ 0·1273 H_2O. C = 59·9; H = 7·1.
$C_{17}H_{24}O_7$ requires C = 60·0; H = 7·0 per cent.

This ester, which is produced almost quantitatively by the process described above, is sharply distinguished from the unmethylated ester (p. 763) by the fact that its alcoholic solution gives no coloration with ferric chloride.

Action of Methyl Alcoholic Potash on Ethyl Trimethylketodicyclopentanetricarboxylate. Formation of the Potassium Salt,

$$Me_2C<\begin{matrix}C(CO_2K)\cdot CMe\cdot CO_2K\\ C(CO_2K)\cdot CO\end{matrix},$$

and Trimethylketodicyclopentanedicarboxylic Acid,

$$Me_2C<\begin{matrix}C(CO_2H)\cdot CMe\cdot CO_2H\\ CH\text{——}CO\end{matrix}.$$

—The pure ethyl ester (20 grams) was mixed with a filtered solution of 20 grams of caustic potash in methyl alcohol and allowed to stand in the cold, when a heavy, crystalline precipitate of a potassium salt gradually formed, the separation being complete in 2 hours. The precipitate was collected, washed with methyl alcohol, dried at 100°, and analysed:

0·3121 gave 0·2186 K_2SO_4. K = 31·4.
$C_{11}H_9O_7K_3$ requires K = 31·6 per cent.

This salt, which evidently has the formula represented at the head of this section, is readily soluble in water, but all attempts to obtain the free tribasic acid were unsuccessful, since the solution of the potassium salt on acidifying is decomposed with evolution of carbon dioxide and formation of *trimethylketodi*cyclo*pentanedicarboxylic acid*. This acid is obtained, by extracting the solution repeatedly with ether, and distilling off the ether, as a colourless solid, which is very soluble in water and crystallises from benzene in lustrous plates melting indefinitely at 70—80°.

These crystals apparently contain water or benzene of crystallisation; on heating, they become yellow and the melting point gradually rises to 146°, when it remains constant, and the substance becomes colourless again.

0·1859 gave 0·3848 CO_2 and 0·0941 H_2O. C = 56·4; H = 5·6.
$C_{10}H_{12}O_5$ requires C = 56·6; H = 5·6 per cent.

The *silver* salt, $C_{10}H_{10}O_5Ag_2$, was obtained on adding silver nitrate to a neutral solution of the ammonium salt as a white precipitate, which on analysis furnished the following results:

0·3214 gave 0·1620 Ag. Ag = 50·41.
$C_{10}H_{10}O_5Ag_2$ requires Ag = 50·57 per cent.

*Trimethylketodi*cyclo*pentanecarboxylic Acid*, $Me_2C<\begin{matrix}C(CO_2H)\cdot CHMe\\ |\\ CH\text{———}CO\end{matrix}$.

When the dibasic acid, described in the last section, is dissolved in a little water and heated in a sealed tube at 180° for 6 hours, it is completely decomposed with elimination of carbon dioxide and formation of the corresponding monobasic acid, the formula of which is given above. This acid separates from water, in which it is only sparingly soluble in the cold, in lustrous plates which melt at 134°.

0·14 gave 0·3297 CO_2 and 0·0898 H_2O. C = 64·2; H = 7·1.
$C_9H_{12}O_3$ requires C = 64·3; H = 7·1 per cent.

The *semicarbazone*, $C_8H_{12}O_2\cdot C{:}N\cdot NH\cdot CO\cdot NH_2$, is precipitated as a sandy powder when an aqueous solution of the acid is boiled with semicarbazide hydrochloride and sodium acetate; it melts with decomposition at about 230°.

0·1408 gave 23·7 c.c. nitrogen at 16° and 746 mm. N = 19·2.
$C_{10}H_{15}O_3N_3$ requires N = 18·7 per cent.

Action of Alcoholic Potash on Ethyl Trimethylketodicyclopentanetricarboxylate. Formation of the Lactone of trans-*Trimethylhydroxybutanetricarboxylic Acid*, $Me_2C<\begin{matrix}C(CO_2H)(CHMe\cdot CO_2H)\\ CH_2\cdot CO\cdot O\end{matrix}$.

It has been mentioned in the introduction (p. 744) that the action of boiling ethyl alcoholic potash on ethyl trimethylketodi*cyclo*pentanetricarboxylate proceeds in quite a different way from that of cold methyl alcoholic potash; in the latter case, the di*cyclo*pentane remains intact, whereas in the former it suffers disruption at two points, yielding the lactone represented above.

The pure ester (50 grams) was mixed with an equal weight of potash dissolved in ethyl alcohol and the solution boiled for 12 hours, when the action was complete. The product was evaporated to dryness to remove alcohol, dissolved in a little water saturated with ammonium sulphate and extracted repeatedly with ether, but, after drying over calcium chloride and distilling off the ether, only a small quantity of a thick gum was obtained. As ether was evidently unable to extract the acid from its aqueous solution, the whole was mixed with sand, evaporated to dryness, and extracted in a Soxhlet apparatus with dry ether. It was then noticed that the ether gradually extracted a white substance which was very sparingly soluble and separated out in the flask, but even after the process had been continued for 4 days the extraction of this white substance was far from complete. When, however, acetone was substituted for ether, very satisfactory results were obtained.

The method we ultimately adopted in extracting this acid from the acidified product of the hydrolysis was to evaporate to dryness and thoroughly extract the dried product in the Soxhlet apparatus with ether, in order to remove a trace of oily impurity soluble in ether and then to extract with pure acetone. On evaporating off the acetone, a large quantity of a solid remained which, after washing with ether melted at 225—227° with evolution of aqueous vapour. When boiled with water, this substance gradually dissolved, and on cooling slowly, large, colourless prisms were deposited which melted at 237° with decomposition.

0·1908 gave 0·3588 CO_2 and 0·1047 H_2O. C = 51·3; H = 6·1.
$C_{10}H_{14}O_6$ requires C = 52·1; H = 6·1 per cent.

This *lactone* of *trimethylhydroxybutanetricarboxylic acid* is a remarkably stable substance; it does not appear to be acted on by dry hydrobromic acid in the cold, and its solution in sodium carbonate may be

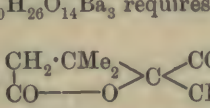
boiled with permanganate for a considerable time without appreciable oxidation taking place. It is unchanged by boiling dilute sulphuric acid, and is not altered by heating with water in a sealed tube at 180°. It is very sparingly soluble in the usual organic solvents, excepting acetone, and dissolves moderately in hot water but only sparingly in the cold.

The *silver* salt, $C_{10}H_{12}O_6Ag_2$, separates from a neutral solution of the ammonium salt, on the addition of silver nitrate, as a white, crystalline precipitate, which dissolves appreciably in hot water and crystallises out on cooling in plates.

0·1967 gave 0·1929 CO_2, 0·0492 H_2O, and 0·0952 Ag.
C = 26·9 ; H = 2·8 ; Ag = 48·4.
$C_{10}H_{12}O_6Ag_2$ requires C = 27·0 ; H = 2·7 ; Ag = 48·6 per cent.

The *barium* salt of the hydroxytricarboxylic acid, $(C_{10}H_{13}O_7)_2Ba_3$, was prepared by dissolving the lactone acid in water, heating to boiling in a Jena flask, and adding clear hot barium hydroxide solution in small quantities at a time, so that the solution was kept always slightly alkaline. A sparingly soluble barium salt gradually separated in the form of a sandy powder, and after boiling for 2 hours (air being carefully excluded from the flask) the salt was collected on the pump, rapidly washed with hot water, and dried at 100°.

0·3910 gave 0·3048 $BaSO_4$. Ba = 45·8.
$C_{20}H_{26}O_{14}Ba_3$ requires Ba = 45·6 per cent.

The *anhydride*,  , may be prepared by boiling the lactonic acid with acetyl chloride for 4 hours. The acid gradually dissolves, and hydrogen chloride is evolved, but the process proceeds very slowly and generally some of the unchanged acid separates on cooling, so that it is necessary to filter the solution and boil the residue again with acetyl chloride. On allowing the solution to evaporate over potash in an exhausted desiccator, large crystals gradually separate: these are collected, ground to a fine powder, and left over potash until the odour of acetic anhydride has entirely disappeared. The substance then melts indefinitely and when treated with benzene a small quantity of a crystalline compound remains undissolved; if this is removed by filtration and the solution concentrated and allowed to stand out of contact with the air, the pure anhydride crystallises out. On analysis:

0·1896 gave 0·3924 CO_2 and 0·1005 H_2O. C = 56·5 ; H = 5·9.
$C_{10}H_{12}O_5$ requires C = 56·6 ; H = 5·6 per cent.

This substance melts at 94—96° and is insoluble in cold sodium

carbonate solution; that it is the anhydride of the *trans*-acid is shown by the fact that when boiled with water it is slowly converted into this acid.

Action of Phosphorus Pentachloride on the trans-*Lactone. Formation of Ethyl Trimethylchlorobutanetricarboxylate,*

$$CO_2Et\cdot CH_2\cdot CMe_2\cdot CCl(CO_2Et)\cdot CHMe\cdot CO_2Et.$$

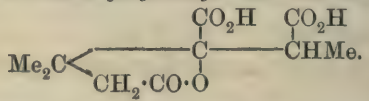
—On heating 2 grams of the lactonic acid with 6 grams of phosphorus pentachloride on the water-bath, it gradually dissolved, and after 2 hours no unchanged substance separated on cooling. The whole was poured into well cooled alcohol and, after standing for some time, water was added, and the oil extracted with ether. The ethereal solution was shaken with sodium carbonate, dried over calcium chloride, and the residual oil allowed to remain over sulphuric acid in a desiccator until free from ether.

0·2494 gave 0·1 AgCl. Cl = 9·9.

$C_{16}H_{27}O_6Cl$ requires Cl = 10·1 per cent.

This substance could not be purified by distillation as it decomposes even under greatly reduced pressures.

Lactone of cis-*Trimethylhydroxybutanetricarboxylic Acid,*

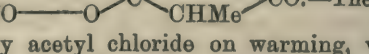


When the *trans*-acid (m. p. 237°) is distilled under 30 mm. pressure, an oil passes over at 267°, which solidifies, on cooling, to a crystalline mass. As the distillate was found to be partly soluble and partly insoluble in dilute sodium carbonate, and therefore evidently consisted of a mixture of acid and anhydride, it was boiled with water, and the solution concentrated and cooled, when microscopic needles separated, which melted at 181° and decomposed with evolution of aqueous vapour at 200°.

0·1834 gave 0·3499 CO_2 and 0·1030 H_2O. C = 52·0; H = 6·2.

$C_{10}H_{14}O_6$ requires C = 52·1; H = 6·1.

This *cis*-acid is much more soluble in water than the *trans*-acid, but like the latter it is a very stable substance, and is only very slowly attacked by boiling alkaline permanganate.

The Anhydride,  .—The *cis*-acid is instantly attacked by acetyl chloride on warming, with evolution of hydrogen chloride, and on evaporating over potash a solid residue is obtained which is quite insoluble in cold sodium carbonate solu-

tion. This anhydride crystallises from benzene in lustrous plates, melts at 131°, and when boiled with water is reconverted into the *cis*-acid.

0·1816 gave 0·3751 CO_2 and 0·0942 H_2O. C = 56·3; H = 5·7.
$C_{10}H_{12}O_5$ requires C = 56·6; H = 5·6 per cent.

When the *cis*-lactonic acid is treated with phosphorus pentachloride and the product poured into alcohol, exactly as in the case of the *trans*-acid, an oil is obtained which decomposes when distilled.

0·2501 gave 0·101 AgCl. Cl = 10·0.
$C_{16}H_{27}O_6Cl$ requires Cl = 10·1 per cent.

This oil is evidently *ethyl trimethylchlorobutanetricarboxylate*, but there is no evidence to show whether this is identical or not with the substance of the same composition obtained from the *trans*-acid.

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LXXXIV.—*Lead Silicates in Relation to Pottery Manufacture.*

By T. E. Thorpe, C.B., F.R.S., and Charles Simmonds, B.Sc.

The present communication is an outcome of certain work undertaken at the instance of the Home Office, in connection with an attempt by that Department to deal with the question of lead-poisoning as it occurs in the pottery industry.

Lead, in one form or another, is largely used in compounding the various glazes employed by potters. By far the most usual form in England is what is technically called "raw" lead. The term includes, by implication, any lead compound which has not been "fritted"—that is, fused with siliceous materials; but practically it comprises only litharge, white lead, and red lead. These substances, especially the two first, are readily dissolved by the acids of the animal organism, such, for instance, as the hydrochloric acid of the gastric juice. When, therefore, they by any means gain access to the alimentary canal or other acid-bearing region of the body, they are attacked by the acid, dissolved, and pass easily into the circulatory system.

Thus the physiological action depends, primarily, upon the solubility of the lead compounds. One of the chief objects of our investigation, therefore, was to obtain if possible some compound of lead which, while serving the practical needs of the potter in respect of such points as

fusibility and expansibility, should at the same time be in respect to its lead nearly insoluble in dilute acids.

In seeking for such compounds, we naturally turned, in the first place, to the silicates of lead. For certain special purposes, indeed, lead silicates are frequently employed by the potter, and attempts have from time to time been made in this country to substitute such silicates for the "raw" lead used in glazes generally. On the Continent, this use of lead silicates is far more common than in England, and it has been generally recognised that their employment has greatly tended to minimise the risk of lead poisoning among pottery workers. In consequence of their more extended use, the conditions required to produce them successfully have received a considerable amount of attention. Indeed, we may at once say that the first insight into the chemical constitution of silicates which should approximate to the ideal character of a "fritt," as these lead compounds are technically termed, was gained by a study of silicates which were found to be in use on the Continent, and were at the same time of a high degree of insolubility. That such silicates were sparingly soluble was generally recognised, but little appears to have been ascertained as to the conditions which determine their insolubility, although it was no doubt surmised that, broadly speaking, it must be dependent upon their chemical nature.

With a view of obtaining light upon the relation of solubility to chemical composition, a number of specimens of lead silicates, both simple and complex, were obtained from manufacturers in the Potteries and on the Continent, and after their solubility as regards lead had been determined, the specimens were analysed to see what information could be gained as to the causes of the difference of solubility shown by the various silicates.

For the solubility determinations, the solvents selected in the earlier stages of the experiments were solutions of hydrochloric, acetic, and lactic acids, of various strengths ranging up to 1 per cent. Afterwards, only a 0·25 per cent. solution of hydrochloric acid was employed; it contains what is considered to be about the average amount of free hydrochloric acid present in the gastric juice. As regards procedure, the method eventually found most practicable for the purpose in view was to shake the finely powdered silicate for an hour with a thousand times its weight of the solvent at the temperature of the room, using for this purpose an agitator worked by a small hot-air motor. The sediment was then allowed to settle for an hour, and the liquid filtered. The quantity of lead which had passed into solution was determined in the filtrate.*

* A note explaining the considerations which led to the particular method adopted is appended. See p. 805.

Any small differences of solubility due to fluctuations of temperature were in the present connection unimportant.

Some of the estimations of the dissolved lead were made by a colorimetric method; but the majority of the determinations were gravimetric, the lead being separated as sulphide and weighed as sulphate.

The first specimens examined included some "fritts," which represented practically the only kind of lead silicate used to any appreciable extent in the Potteries. This compound approximates to a simple monosilicate of lead, PbO,SiO_2. It contains, however, the small quantities of alumina, lime, and alkalis usually associated with the silica in the flint from which the compound is made, one sample giving on analysis:

Silica	25·11 per cent.
Lead monoxide	70·40 ,,
Alumina	0·88 ,,
Lime	0·92 ,,
Magnesia	0·13 ,,
Alkalis	1·91 ,,
	99·35 ,,

At the time when our inquiry began, this crude monosilicate was held to be a satisfactory substitute for "raw" lead, on the assumption that it was much less soluble than the latter. Contrary to expectation, it was found to yield practically the whole of its lead to the action of 0·25 per cent. hydrochloric acid.

Two different preparations gave the following figures:

Specimen.	PbO present.	PbO dissolved by 0·25 per cent. HCl.	Calculated on the total PbO present.
1	71·2 per cent.	70·0 per cent.	98·3 per cent.
2	70·4 ,,	67·3 ,,	95·6 ,,

It is evident, therefore, that so far as the solubility of the lead is concerned, the advantage which the simple monosilicate was supposed to possess over "raw" lead had no foundation in fact.

Turning our attention therefore to the complex silicates, we obtained from English makers two silicates having the following composition:

	No. 3.	No. 4.
Silica	37·62 per cent.	35·66 per cent.
Lead monoxide	37·92 ,,	45·77 ,,
Alumina	8·24 ,,	10·04 ,,
Lime	10·83 ,,	1·16 ,,
Magnesia	0·08 ,,	0·14 ,,
Alkalis	3·72 ,,	7·09 ,,
	98·41	99·86

The quantities of lead oxide dissolved from these were:

From No. 3..... 28·0 per cent.
„ 4..... 10·8 „

Two points are brought out by these results. In the first place, the solubility of the lead is very much smaller in both specimens than in the simple monosilicates Nos. 1 and 2. Secondly, it will be seen that No. 4, with the larger percentage of lead oxide in its composition, gives to the action of acid a much smaller amount of lead than does No. 3. This was the first illustration we obtained of a principle elucidated more fully further on, namely, *that the quantity of lead dissolved bears no necessary relation to the quantity of lead in the silicate.*

Extending the inquiry, we next examined three "fritts" containing much smaller quantities of lead than the foregoing, and including also boric oxide as a constituent. The composition and solubility of these three borosilicates are given below:

	No. 5 (English).	No. 6 (Belgian).	No. 7 (Dutch).
Silica	49·67 per cent.	52·94 per cent.	53·16 per cent.
Lead monoxide	16·23 „	22·44 „	18·97 „
Alumina	10·34 „	7·62 „	8·06 „
Lime	8·54 „	8·82 „	8·96 „
Magnesia	0·19 „	0·12 „	0·11 „
Alkalis	9·20 „	3·99 „	4·86 „
Boric oxide.....	5·83 (difference)	3·82 „	5·88 (difference)
	100·00	99·75	100·00
Lead oxide dissolved by 0·25 HCl	1·70 per cent.	0·65 per cent.	1·20 per cent.

Here the solubility of the lead, especially in the Belgian borosilicate, is remarkably small compared with what was shown by the previous specimens.

Now in round numbers these examples differ from Nos. 3 and 4 chiefly in containing about 15 per cent. more silica and about 20 per cent. less lead monoxide. Moreover, they have from 4 to 6 per cent. of boric oxide, which is not present at all in Nos. 3 and 4.

The question therefore suggested itself: Was the factor determining the insolubility of the lead to be sought in a high percentage of silica, or in a low proportion of lead oxide? Or was it, as a possibility without very much likelihood, to be found in the introduction of boric oxide into the "fritt"?

The next specimen analysed gave us the answer to these questions, and it was an unmistakable negative. This specimen was a Swedish "fritt," for which the figures are:

No. 8.

Silica	44·74 per cent.
Lead monoxide	44·06 „
Alumina	5·47 „
Lime	0·89 „
Magnesia	0·13 „
Alkalis	3·37 „
Boric oxide	Absent
Loss on heating	0·45 „
	99·11
Lead oxide dissolved by 0·25 per cent. HCl...	2·10 per cent.

Although the solubility of the lead is in this case somewhat greater than in Nos. 5 to 7, it is a quantity of the same order as the figures for these, and for the purpose of the moment may be classed with them.

Here, then, it was plain that the low solubility could not be due to the presence of boric oxide, for this constituent is absent. Nor was it due to a high percentage of silica, which is here much less than in Nos. 5, 6, and 7. Nor, again, could it be attributed to a low proportion of lead oxide, because of this there is twice as much as in the three previous examples.

Comparing in this way the results of a number of analyses, it becomes evident that the solubility of the lead does not depend in a simple manner upon any one of the constituents. We append for this purpose a table showing the composition and solubility of a number of silicates (see p. 805); here we will illustrate the point by reference to the lead oxide only.

I. *Solubilities practically the same*: amounts of lead oxide in the silicates very different.

Silicate.	Percentage of PbO in the silicate.	Solubility of the PbO Percentage on silicate.
Specimen 7*a* (Dutch)	18·0	all less
„ (English)	40·4	than
„ „	52·3	0·5
„ „	41·3	0·7
„ 6 (Belgian)	22·4	0·7

II. *Solubilities very different*: amounts of lead oxide in the silicates practically the same.

Specimen 3 (English)	37·9	28·0
„ 9 „	36·2	1·4
„ 4 „	45·8	10·8
„ 8 (Swedish)	44·1	2·1

The same principle holds for each of the other oxides, whether basic or acidic. Generally, the quantity of lead dissolved by the solvents used bears no necessary proportionality to the percentage of any constituent of the silicate.

Primarily, and in the main, the insolubility of the lead depends, not upon any one oxide or group of oxides, but upon the maintenance of a certain proportion between the whole of the basic oxides on the one hand, and the whole of the acidic oxides on the other. This proportion, as will be shown later, becomes eventually referable to the ultimate hypothetical acids from which the silicates may be considered to be derived. Meanwhile, one method of formulating this relation is as follows.

Proceeding as in the ordinary calculation of a silicate formula, we divide the percentage weight of each oxide by its molecular weight. The quotient expresses the relative number of molecules of that oxide present in a definite weight of the silicate. Adding the quotients for the acidic oxides gives the total number of acidic molecules; and similarly for the basic molecules. If we then take the ratio of the former sum to the latter for each silicate, we get the following table:

Silicate.	Value of ratio. No. of acidic mols. / No. of basic mols.	Solubility. Percentage on silicate.
1	2·75	Traces.
2	2·56	,,
3	2·49	1·2
4	2·43	0·7
5	2·42	2·4
6	2·37	2·1
7	2·35	0 2
8	2·20	0·2
9	2·18	0·6
10	2·15	0·2
11	2·10	0·2
12	2·02	1·7
13	2·06	0·7
14	1·98	0·8
15	1·98	0·4
16	1 95	3·0
17	1·93	1·5
18	1·89	2·0
19	1·44	40·1
20	1·43	39·5
21	1·42	10·8

Silicate.	Value of ratio. No. of acidic mols. / No. of basic mols.	Solubility. Percentage on silicate.
22	1·33	5·1
23	1·27	28·0
24	1·20	70·3
25	1·13	67·3
26	0·90	70·0

The table shows some aberrations which have a certain significance; these will be discussed further on. Disregarding them for the moment, we see that so long as the value of this ratio is higher than or approximately equal to 2, the solubility of the lead is small, being for the most part much below 2 per cent., and only in one instance reaching 3 per cent. That is, the solubility is small so long as there are present two molecules or more of acidic oxides to each molecule of basic oxide. When the ratio falls much below 2, the quantity of lead dissolved begins rapidly to increase.

In this connection, it is interesting to recall an observation made some seventy years ago by Faraday, during his classical researches upon heavy glass. In his paper entitled "On the Manufacture of Optical Glass," published in the *Philosophical Transactions* for 1830, Faraday states that glass made of equal weights of silica and lead oxide does not become dull when exposed to the action of hydrogen sulphide, but if 8 parts of this glass are fused with 1 part of potash, the glass produced becomes tarnished on exposure to the sulphydric acid. Now, in the former case the ratio of $\frac{\text{acidic molecules}}{\text{basic molecules}}$ is 3·7, whereas in the case of the glass attacked by hydrogen sulphide the ratio is 2·3—or, if allowance be made for the small quantities of bases generally associated with the silica in sand, about 2·0. This glass would therefore in the table fall with the silicates which yield small quantities, though only small quantities, of lead to the action of dilute hydrochloric acid. Faraday appears to have regarded the tarnishing of the glass as due to some special influence of the alkali, *qua* alkali: it may, however, have been simply an illustration of the principle just developed, namely, that the more basic the silicate, the more readily is the lead attacked by acids.

The relation between acidic and basic oxides may be formulated in another manner, which may be thus stated: Express the percentage of each basic oxide in terms of some one of them, say PbO, and that of the boric oxide in terms of SiO_2. Then take the ratio of the sum of the basic oxides to that of the acidic oxides.

The table previously given suggests that, so far as influence upon the solubility of the lead is concerned, one molecule of the sesquioxide

Al_2O_3 may replace one molecule of a monoxide base. We may therefore calculate the ratio first with Al_2O_3 put = PbO, and next with Al_2O_3 put = 3PbO, and compare the results, which are given with the solubilities in the following tables:

Arranged in order of increasing values of the ratios.

(i). With Al_2O_3 put = PbO.			(ii). With Al_2O_3 put = 3PbO.		
Silicate.	Ratio.	Solubility of PbO.	Silicate.	Ratio.	Solubility of PbO.
1	1·34	traces	1	1·90	traces
2	1·44	,,	2	2·01	,,
3	1·50	1·2	6	2·10	2·1
4	1·52	0·7	3	2·11	1·2
6	1·56	2·1	4	2·12	0·7
7	1·57	0·2	10	2·19	0·2
8	1·68	0·2	15	2·34	0·4
9	1·70	0·6	8	2·41	0·2
10	1·73	0·2	17	2·41	1·5
11	1·77	0·2	18	2·48	2·0
13	1·80	0·7	13	2·56	0·7
12	1·82	1·7	7	2·60	0·2
15	1·83	0·4	11	2·64	0·2
14	1·87	0·8	16	2·64	3·0
16	1·91	3·0	12	2·65	1·7
17	1·92	1·5	14	2·76	0·8
18	1·97	2·0	9	2·78	0·6
20	2·59	39·5	24	3·27	70·8
19	2·59	40·1	25	3·43	67·3
21	2·61	10·8	22	3·55	5·1
22	2·79	5·1	21	3·84	10·8
23	2·92	28·0	23	3·88	28·0
24	3·09	70·3	20	3·90	39·5
25	3·26	67·3	19	3·92	40·1
26	3·80	70·0	26	4·10	70·0

By either method of computation the same compounds fall into the same groups, but the first method gives somewhat the more consistent results for the higher solubilities.

This, indeed, was so marked in the silicates first examined as to lead to the provisional adoption, for working purposes, of this method of expressing the relation in question. The values of the ratio, bases : acids, were calculated first with $Al_2O_3 = 3PbO$ and $2B_2O_3 = 3SiO_2$; next with $Al_2O_3 = 3PbO$ and $B_2O_3 = SiO_2$; then with $Al_2O_3 = PbO$ and $B_2O_3 = SiO_2$. The last method alone was found to give concordant results when the amounts of lead dissolved were large, as will be seen from the following table:

Silicates.	Percentage of PbO dissolved, calculated on PbO in silicate.	Value of ratio.		
		I. With $Al_2O_3=3PbO$, and $2B_2O_3=3SiO_2$.	II. With $Al_2O_3=3PbO$, and $B_2O_3=SiO_2$.	III. With $Al_2O_3=PbO$, and $B_2O_3=SiO_2$.
L	5·6	2·02	2·11	1·50
G	6·6	2·54	2·65	1·83
N	23·8	3·84	3·84	2·62
E	60·4	3·88	3·88	2·93
F	99·6	3·43	3·43	3·27

Subsequent experience has confirmed this, to the extent at least that the method III gives the most consistent results. At the same time, it must be borne in mind that the special point now being advanced is not that the quantity of lead dissolved is directly proportional to any function of the ratio, but that the solubility is small below a certain value of the ratio, and becomes considerable when this value is much exceeded. The value in question is about 2 by the first method of calculation given on p. 798, and about $2\frac{3}{4}$ by the second.

This condition, then—the maintenance of the proper relation between the basic oxides and the acidic oxides—is the primary factor governing the insolubility of the lead in the silicate.

Subsidiary factors may exist in the possible different states of combination in which alumina and boric oxide may occur in the silicate.

It is conceivable that in some cases the alumina may act as an acid constituent. In such cases, the amount of lead dissolved would presumably be less than indicated from the value of the ratio. Possibly the compound No. 22, in the table (p. 798), is an instance of this.

As regards boric oxide, since lead borate is readily attacked by acids it might perhaps be expected that the borosilicates would show some traces of this property, as compared with silicates containing no boric oxide. But, as a matter of fact, the highest quantities of boric oxide met with (from 4 to 6 per cent.) were contained in those specimens which yielded least lead to the action of the solvents. It does not, however, follow that in these cases the boric oxide exerted any influence in promoting the insolubility of the lead; because the specimens in question all contained high percentages of silica, and the stability of the compounds may have been due to this cause, irrespective of any special influence of the boron. In the case of silicates in which the relation of basic oxides to acidic oxides is such as to bring the compounds near the border-line between the easily-attackable and the

more resistant, it is quite possible that the substitution of any appreciable quantity of boric oxide for a corresponding quantity of silica might result in the compounds showing, not an increased, but a decreased resistance to the action of acids. The silicates 19 and 20 in the table on p. 798, both of which contain boric oxide, may perhaps be instances of this.

Pending further work, the precise influence of these subsidiary factors remains somewhat obscure. But though these are matters of considerable theoretical interest, the point which is of chief practical moment may, we think, be regarded as completely established. By keeping the relative proportions of bases and acids sufficiently within the limits indicated, sparingly soluble silicates are always obtained, and the influence, whatever it may be, of these minor factors does not then come into play.

A second condition, governing the smaller quantities of lead extracted, may also be mentioned. Dealing now only with the specimens 1 to 17, all of which conform to or are very near the limiting ratio, whichever method of calculation is adopted, it will be seen that in these the solubility of the lead, though never large, varies very erratically. In some instances mere traces are dissolved; in others, the quantity is from 1 to 3 per cent.

The explanation of this was suggested by considering the results of the following experiments:

	Lead oxide dissolved.	
	With 0·25 per cent. HCl.	With 0·05 per cent. HCl.
From specimen K.....	0·65 per cent.	0·60 per cent.
„ „ L.....	1·20 „	1·10 „

Here the acid used in one case is five times as strong as in the other, but it extracts scarcely any more lead. This indicated that although the great bulk of each specimen consisted of silicate which was not attacked even by the stronger acid, it nevertheless contained a small quantity of some compound of lead, probably admixed with it, or perhaps in some loose state of combination, which was readily dissolved even by the weaker solvent. Most probably this may have been due to the process of fusion not having been sufficiently prolonged to effect the complete chemical changes required. But, let the explanation be what it may, the experiments suggested that in those specimens which conformed to the ratio indicated, yet still yielded one or two per cent. of lead oxide to the solvent, the greater part of the lead compound thus dissolved was in this admixed or loosely combined form. If so, it could be removed by treatment with acid, and the residue should then be practically insoluble.

This supposition was verified experimentally, the results of some

typical experiments being given below. The observation has a practical value, since it shows the manufacturer that by simply grinding certain moderately soluble "fritts" with dilute acid, he can obtain a product which yields mere traces of lead to the action of such solvents as we are here concerned with.

Experiments upon the Treatment of Lead Silicates with Dilute Solution of Hydrochloric Acid.

Silicates which yielded amounts of soluble lead oxide ranging up to 2 per cent., were separately shaken with 500 times their weight of 0·25 per cent. hydrochloric acid for six hours. The dissolved portion was analysed, and the undissolved residue tested for its solubility as regards lead.

Silicate.	Amount of silicate dissolved, per cent.		Amount of silicate dissolved, per cent.
1	3·02	5	3·41
2	4·35	6	2·72
3	3·70	7	3·40
4	5·97		

In all cases, the dissolved portion consisted largely of lead oxide. A typical analysis is adduced to show the general character of the substances dissolved.

Lead silicate No. 7. Composition of the dissolved portion:

Silica	2·1	per cent.
Lead monoxide	67·6	,,
Alumina	10·3	,,
Lime	5·3	,,
Magnesia	Traces	,,
Alkalis Na_2O	7·9	,,
Alkalis K_2O	6·8	,,
Boric oxide	Traces	,,
	100·0	

In the undissolved residue, the percentage of lead oxide is but little less than in the original silicate. But the amount of this lead now extracted by the standard solvent is only about one-third to one-eighth of that yielded previously.

Thus the conditions upon which the production of nearly insoluble lead silicates depends are:

Firstly, the preservation of the proper relation between the acidic and the basic constituents, as exemplified above.

Silicate.	Lead oxide present.		Lead oxide dissolved.	
	(i) In the original.	(ii) In the residual silicate.	(i) From the original.	(ii) From the residual silicate.
1	22·4 per cent.	21·8 per cent.	0·7 per cent.	traces
2	19·0 ,,	18·0 ,,	1·2 ,,	,,
3	53·2 ,,	52·3 ,,	2·0 ,,	0·4 per cent.
4	49·3 ,,	47·5 ,,	1·5 ,,	0·2 ,,
5	24·5 ,,	24·0 ,,	0·6 ,,	0·2 ,,
6	41·4 ,,	40·7 ,,	0·8 ,,	0·2 ,,
7	41·3 ,,	40 4 ,,	0·7 ,,	0·2 ,,

Secondly, the fusion of the materials for such a time and in so thorough a manner as to allow of the chemical reactions being completed.

To these may be added, in certain cases, the treatment of the silicate with acid in order to extract small quantities of admixed or loosely combined lead compounds from the bulk of the product.

The following propositions are of both practical importance and theoretical interest.

Provided that the foregoing conditions are satisfied, then, without prejudice to the insolubility in the standard solvent of the lead in the silicate:

(1) The quantity of lead oxide in the silicate may have any value up to 50 or 55 per cent., or even higher.

(2) The other bases (lime, alumina, and alkalis) may vary considerably, replacing one another, and also the lead oxide, within very wide limits. This is illustrated by the following table:

Table showing that the nature of the basic oxides has little or no effect upon the amount of lead dissolved.

Silicate.	Percentages. PbO.	Al_2O_3.	CaO.	Alkalis.	Lead oxide dissolved. Percentage on silicate.
L_1	19·0	8·1	9·0	4·9	1·2
G	16·2	10·3	8·5	9·2	1·7
R	44·1	5·5	0·9	3·4	2·1
Flint glass ...	44·6	0·4	0·5	8·1	2·4

(3) The influence of boric oxide, irrespective of that of the silica with which it may be associated, still remains to be ascertained; but it has been pointed out that boric oxide up to 6 per cent., the highest

amount met with in the specimens examined, may in certain cases be present without apparently exercising any special influence in promoting the solubility of the lead.

Formulæ of the Lead Silicates.—As might be expected, the silicates dealt with do not as a rule give complete formulæ of a simple character. But by grouping together the mutually replaceable oxides, and then calculating the ultimate acids corresponding to the formulæ thus obtained, the silicates are found to be theoretically derivable from acids which approximate to the three following :

	Atomic ratio Si : O
Meta-silicic acid, H_2SiO_3	1 : 3
Meta-polysilicic acid, $H_4Si_3O_8$	3 : 8
Meta-disilicic acid, $H_2Si_2O_5$	2 : 5

Moreover, it will be seen that all those silicates which yield lead in quantity to the standard solvent are referable to the first acid ; whilst all those of slight solubility are derived from the other two.

It is to be remembered that the small quantity of easily dissolved material previously mentioned is probably an admixture. With this reservation, the following groups of formulæ may be given as closely representing the soluble and insoluble specimens respectively.

GROUP I.—*With large amounts of soluble lead oxide. Meta(mono)silicates.* Si : O = 1 : 3.

Specimen.	Lead oxide dissolved. Per cent.	Formula. RO = $(Pb,Ca,Mg,Na_2,K_2)O$.	Type, $xH_2O,ySiO_2$.	Atomic ratio, Si : O.
1	5·1	$32RO,5Al_2O_3$, – $49SiO_2$	$47H_2O,49SiO_2$	1 : 2·96
2	10·8	10 ,, 3 ,, – 18 ,,	19 ,, 18 ,,	1 : 3·05
3	28·0	5 ,, 1 ,, – 8 ,,	1 ,, 1 ,,	1 : 3·00
4	39·5	18 ,, 7 ,, – 36 ,,	13 ,, 12 ,,	1 : 3·08
5	40·1	8 ,, 3 ,, – 16 ,,	17 ,, 16 ,,	1 : 3·06
6	67·3	80 ,, 2 ,, – 93 ,,	86 ,, 93 ,,	1 : 2·93
7	70·3	32 ,, 1 ,, $3B_2O_3$, 36 ,,	70 ,, 81 ,,	1 : 2·86

GROUP II.—*With small amounts of soluble lead oxide. Polysilicates and disilicates.*

Specimen.	Lead oxide dissolved. Per cent.	Formula. RO = (Pb,Ca,Mg,Na_2,K_2)O.	Type, $xH_2O,ySiO_2$.	Atomic ratio, Si : O.
		Polysilicates, Si : O = 3 : 8.		
1	0·2	10RO,5Al_2O_3,2B_2O_3,34SiO_2	25H_2O,37SiO_2	3 : 8·04
2	0·2	6 ,, 2 ,, 17 ,,	12 ,, 17 ,,	3 : 8·10
3	0·2	7 ,, 2 ,, – 20 ,,	13 ,, 20 ,,	3 : 7·95
4	0·4	19 ,, 3 ,, – 44 ,,	7 ,, 11 ,,	3 : 7·92
5	0·6	28 ,, 13 ,, 5B_2O_3,84 ,,	134 ,, 183 ,,	3 : 8·19
6	0·7	15 ,, 4 ,, – 39 ,,	9 ,, 13 ,,	3 : 8·07
7	0·8	23 ,, 7 ,, – 60 ,,	11 ,, 15 ,,	3 : 8·20
8	1·5	21 ,, 3 ,, – 46 ,,	15 ,, 23 ,,	3 : 7·95
9	1·7	21 ,, 6 ,, 5B_2O_3,50 ,,	78 ,, 115 ,,	3 : 8·04
10	2·0	60 ,, 9 ,, – 130 ,,	87 ,, 130 ,,	3 : 8·01
11	3·0	17 ,, 4 ,, – 41 ,,	29 ,, 41 ,,	3 : 8·10
		Disilicates, Si : O = 2 : 5.		
1	traces	4RO, Al_2O_3, B_2O_3,13SiO_2	14H_2O,29SiO_2	2 : 4·96
2	,,	33 ,, 8 ,, 6 ,, 99 ,,	19 ,, 36 ,,	2 : 5·06
3	0·2	7 ,, 1 ,, – 17 ,,	10 ,, 17 ,,	2 : 5·18
4	0·7	32 ,, 8 ,, 6B_2O_3,91 ,,	14 ,, 25 ,,	2 : 5·12
5	1·2	4 ,, 1 ,, 1 ,, 11 ,,	14 ,, 25 ,,	2 : 5·12
6	2·1	5 ,, 1 ,, – 14 ,,	4 ,, 7 ,,	2 : 5·14
7	2·4	5 ,, — – 12 ,,	5 ,, 12 ,,	2 : 4·83

Several of the foregoing specimens contain boric oxide, ranging in amount from 0·3 to 6·1 per cent. To simplify the formulæ, which would otherwise often be very cumbersome and unwieldy, the smaller quantities of this oxide, about 1 per cent. or less, have been included with the SiO_2.

Two examples of more detailed formulæ are appended. The first is that of a very soluble silicate, the second that of an insoluble one.

(1) $2(Na,K)_2O,(Ca,Mg)O,29PbO,Al_2O_3,3B_2O_3,36SiO_2$.
(2) $2(Na,K)_2O,6(Ca,Mg)O,4PbO,3Al_2O_2,2B_2O_3,37SiO_2$.

Table showing the composition of various lead silicates, with the amount of lead oxide dissolved from them by 0·25 per cent. solution of hydrochloric acid.

Silicate, arranged in order of increasing solubility.	PbO dissolved by 0·25 per cent. HCl. Per cent. of silicate.	Percentage composition.						
		PbO.	CaO.	MgO.	$(Na,K)_2O$.	Al_2O_3.	B_2O_3.	SiO_2.
1	traces	21·83	8·54	0·12	3·80	7·43	3·84	54·44
2	,,	18·04	8·43	0·06	4·39	7·71	6·14	55·23
3	0·7	22·44	8·82	0·12	3·99	7·62	4·07	52·94
4	1·2	18·97	8·96	0·11	4·86	8·06	5·88	53·16
5	1·7	16·23	8·54	0·19	9·20	10·34	5·83	49·67
*6	2·0	—	—	—	—	—	—	37·88
7	2·1	44·06	0·89	0·13	3·37	5·47	—	44·74
8	2·4	44·64	0·53	—	8·05	0·36	—	45·48
9	3·0	41·13	2·08	0·15	5·88	7·15	—	43·61
*10	5·1	—	—	—	—	—	—	29·78
11	10·8	45·77	1·16	0·14	7·09	10·04	—	35·66
12	28·0	37·92	10·83	0·08	3·72	8·24	—	37·62
13	39·5	46·78	1·98	0·24	2·80	11·52	1·17	33·75
14	40·1	48·70	0·83	0·30	3·59	10·97	1·35	33·43
15	67·3	70·40	0·92	0·13	1·91	0·88	—	25·11
16	70·3	70·25	0·51	0·06	1·59	1·08	2·64	23·87

* Inserted to show that the solubility of the lead oxide does not depend simply upon the proportion of SiO_2. The full details of these, as of some others mentioned, in the paper, are withheld from publication, by desire of the manufacturers.

Note on the Method adopted for Determining the Quantity of Lead Extracted in the foregoing Experiments.

One hour's shaking with the solvent at the ordinary temperature with a subsequent hour's settling, was found long enough to dissolve the whole of the lead from easily soluble silicates. From sparingly soluble silicates it dissolved nearly, though not quite, as much lead as 2 hours' shaking. It thus served to discriminate between the two classes of compounds, and was a practical working length of time to adopt.

The common temperature was chosen, as being a more practicable temperature for laboratory purposes than that of blood heat, and less liable to variation during experiments. No doubt somewhat less lead is dissolved from the sparingly soluble silicates under these conditions than would be dissolved at the blood temperature.

With regard to the quantity of acid employed, a quantity equal to one thousand times the weight of the solid was chosen, for two reasons; first, in order that under all circumstances an excess of acid should

be present; and secondly, in order that the excess should be so great as to obviate any considerable weakening of the acid through the neutralising action of the soluble constituents of the silicate.

With regard to the necessity for the use of an excess of acid, an observation of some interest was made during the course of the experiments. A series of solubility determinations was undertaken, in which the various lead silicates were employed much in excess of the acid used as a solvent. Remembering that the monosilicates easily yield the whole of their lead to an excess of 0·25 per cent.—and indeed to 0·05 per cent.—hydrochloric acid, it might have been expected that, even when the solvent was not in excess, it would still dissolve as much lead as would correspond approximately to the quantity of acid present. But on testing the solution, small amounts only of lead were found —at most a few centigrams—instead of the 0·76 gram which corresponded to neutralisation of the acid. For example, 10 grams of silicate, containing 7·04 grams of lead monoxide, were shaken with 100 c.c. of 0·25 per cent. HCl for 48 hours. The lead oxide in solution was found to be only 0·03 gram, although the quantity which the solution might have dissolved, if solution had proceeded until the acid was neutralised, was 0·76 gram.

This occurred only when hydrochloric acid was used, and not with lactic or acetic acids. It was, therefore, surmised that what had happened was this: The silicate was at first attacked, and lead dissolved until the acid was neutralised. Then the lead chloride in solution, reacting with the excess of lead silicate, formed with it an insoluble compound, and so was withdrawn from solution. The reaction may have consisted in the decomposition of the silicate into silica or silicic acid and lead oxide, the latter then combining with the lead chloride to form an insoluble lead oxychloride analogous to mendipite; or it may perhaps have taken the form of a direct addition of lead chloride to the silicate, resulting in the formation of a chlorosilicate of some such type as the mineral nasonite, $5PbO,PbCl_2,4CaO,6SiO_2$. The precise nature of the insoluble product was not determined, but the correctness of the general explanation was established by the following experiments.

A solution of lead chloride was prepared, containing per 100 c.c. 0·8594 gram of lead, calculated as monoxide. 10 grams each of litharge, white lead, and lead monosilicate were separately shaken with 100 c.c. of the lead chloride solution for 48 hours. The quantity of lead remaining in solution was then determined. It was found that nearly the whole of the lead chloride had been taken out of solution by the litharge and lead silicate, and 90 per cent. of it by the white lead.

In the case of the litharge, the result was only what was expected,

Action of lead compounds upon a saturated solution of lead chloride.

Compound.	Weight of lead, calculated as oxide, contained in the quantity of lead chloride used (100 c.c.).	Weight of lead, calculated as oxide, remaining in solution after agitation with lead compounds.	Percentage of the lead removed from the solution of lead chloride.
10 grams of Litharge	0·8594 gram	minute traces	100·0
White lead	,, ,,	0·0847 gram	90·1
Lead monosilicate (crude commercial silicate)	,, ,,	0·0156 ,,	98·2

but it was rather surprising to find that the silicate reacted more readily than white lead.

The facility of reaction shown by the silicate raised at first some suspicion that the specimen might have contained more or less lead oxide, which had escaped combination with the silica during preparation. Subsequent experiments, however, showed that this was not the case. Lead monoxide, when heated with olive oil, saponifies it. The specimen of lead silicate was found to have no saponifying action; hence it contained no admixed lead monoxide.

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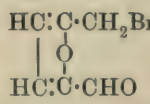
LXXXV.—*Derivatives of Methylfurfural.*

By Henry J. Horstman Fenton, F.R.S., and Miss Mildred Gostling, B.Sc.

In previous communications (Trans., 1898, **73**, 554; 1899, **75**, 423), the authors have described the isolation, properties, and constitution of bromomethylfurfural, $C_6H_5O_2Br$. It was shown that this beautifully crystalline substance results from the action of hydrogen bromide on ketohexoses, such as lævulose and sorbose, or on carbohydrates, which are capable of giving rise to ketohexoses on hydrolysis, such as cane sugar or inulin, and that it may be obtained in a similar manner from various forms of cellulose (Trans., 1901, **79**, 361). The bromine in this compound is extremely reactive, so that it may be quantitatively estimated by direct precipitation with silver nitrate in the cold; the substance itself is hydrolysed by boiling water, in presence of barium

carbonate, giving the corresponding hydroxy-compound; and by oxidation with silver oxide yields the ω-hydroxypyromucic acid previously obtained by Hill and Jennings from the corresponding bromo-acid.

From these considerations, it is evident that the bromine occupies the ω-position, that is, it is present in the side chain and not in the main nucleus, the constitution of the compound being represented by the formula



Owing to the important relations of this compound to the carbohydrate family, and the bearing which its formation has upon questions in vegetable physiology, the authors have considered it advisable to make a further study of its derivatives, and it will be shown that owing to the extremely reactive nature of the substance it is capable of many interesting transformations.

The group or radicle $O{:}CH{\cdot}C_4H_2O{\cdot}CH_2$ has evidently considerable permanence or stability, and it would be a matter of convenience if a simple name were given to it, as has been done in the case of benzyl and other analogous radicles.

Chloromethylfurfural, $O{:}CH{\cdot}C_4H_2O{\cdot}CH_2Cl$.—Recent experiments show that this compound may be produced by the action of hydrogen chloride on ketohexoses and on cellulose in a manner altogether similar to that employed in preparing the bromo-derivative, but that in the first case the action takes place more slowly, and the product is in the first instance more difficult to crystallise.

When lævulose, for example, is treated with hydrogen chloride under ether, there is at first no apparent change except that the solid tends to cake together. After standing for some hours, the mixture becomes pink or purple, but the colour is very much less intense than that given by the action of hydrogen bromide. In the latter case, the action begins almost immediately, and a very intense purple colour is developed within about 30 minutes.

In order to prepare the chloro-derivative, 'commercial' lævulose is covered with dry ether, and the mixture, surrounded by ice, is saturated, or nearly saturated, with dry hydrogen chloride. It is then allowed to stand for a day or two, and the resulting purple mixture is neutralised with sodium carbonate in the manner previously described for the preparation of the bromo-derivative. This neutralisation process is somewhat tedious owing to the large quantity of hydrogen chloride which is necessarily present, but the operation may be economised without much loss by pouring off the ethereal part and shaking it with a small quantity of water, keeping the mixture cool,

and again extracting this aqueous solution two or three times with ether. Only the ethereal extracts and the remaining solid are then neutralised, the aqueous solution being neglected. The excess of acid may also be removed by drawing a current of air through the mixture slightly warmed on a water-bath.

The solid portion is then also extracted with ether, the joint ethereal solutions are dried over calcium chloride, and the ether is then distilled off. The yellow oil or syrup which remains generally refuses to crystallise, but when taken up with hot light petroleum and allowed to stand in a cold place it slowly deposits long, colourless, transparent prisms. In some cases, the substance separates again as an oil, but after this purification it soon sets to a crystalline mass on cooling and stirring, or, better, by sowing with a trace of either the chloro- or bromo-derivative.

The purified substance crystallises extremely well from solvents, whereas in the presence of impurities it exhibits, like the bromo-derivative, a great tendency to remain in a superfused condition. This fact, together with its low melting point, accounts for the difficulty first experienced in isolating it, the experiments having been made in hot weather.

In properties, the chloro-derivative very closely resembles the bromo-derivative, and the crystals appear to be isomorphous. It dissolves very easily in ether, alcohol, chloroform, or carbon tetrachloride, but is only sparingly soluble in hot light petroleum. It melts to a colourless liquid at 37—38°, that is, about 22° lower than the bromo-derivative; at a somewhat higher temperature, if cautiously heated, it vaporises unchanged, giving a colourless liquid which immediately crystallises when touched with a crystal of the substance.

For analysis, it was recrystallised from dry ether and dried in a vacuum desiccator.

0·1459 gave 0·2647 CO_2 and 0·0445 H_2O. C = 49·47; H = 3·38.
0·3650 „ 0·3600 AgCl. Cl = 24·40.
$C_6H_5O_2Cl$ requires C = 49·82; H = 3·46; Cl = 24·56 per cent.

The halogen in this compound is, like that in the bromo-derivative, extremely reactive, so that it may be quantitatively estimated by direct precipitation by silver nitrate in aqueous alcoholic solution.

From cellulose, the compound may be prepared in the same way as the bromo-derivative (*loc. cit.*), and the product in this case usually crystallises directly from the first extraction without previous purification with light petroleum. Using carbon tetrachloride as solvent, saturated at about 0° with hydrogen chloride, and heating for two hours in a water-bath, 50 grams of Swedish filter paper gave 5·2 grams of pure crystals of the chloro-derivative. The product was in every way

identical with that prepared from lævulose; it melted at the same temperature, and the following result was obtained on analysis:

0·3483 gave 0·3448 AgCl. Cl = 24·48 per cent.

It is evident that this is a highly economical way of obtaining the substance, and the yield may probably be considerably increased by longer heating and by further modification of the details.*

Mixtures producing hydrogen chloride may be substituted for the gas itself; thus, for example, a good yield is obtained from cellulose by using a mixture of phosphoryl chloride with about the calculated quantity of water and carbon tetrachloride as solvent. The substance is produced also by the direct action of dry hydrogen chloride on the carbohydrate without the use of a solvent, but the results are not so satisfactory.

When the chloro-derivative is dissolved in strong acetic acid and mixed with excess of phenylhydrazine acetate, a very voluminous, pale yellow or buff precipitate is immediately produced. This, after washing with acetic acid and then with water, contains no chlorine. It appears to consist of more than one substance, since only a part is soluble in benzene or ether, the residue being nearly insoluble even in boiling alcohol.

On adding light petroleum to the benzene or ether solution, an orange-yellow, flocculent precipitate separates which, after drying in a water-oven, melts at 118—120°. This product is being further investigated.

It seems not at all unlikely that a certain amount of the chloro-derivative may be formed in the process usually employed for the estimation of furfural in carbohydrates, &c., and in this case it is evident that its presence would considerably vitiate the results obtained by the phenylhydrazine method.

Acetoxymethylfurfural, $O{:}CH{\cdot}C_4H_2O{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_3$.—This substance is readily obtained by dissolving the bromo-compound in glacial acetic acid and adding excess of silver acetate; after warming and shaking for a short time, until the solution ceases to react with silver nitrate, the solution is filtered and allowed to evaporate in a vacuum desiccator over solid potash. The resulting syrup sets to a crystalline mass on stirring, and the product, after recrystallisation first from dry ether and then from boiling light petroleum, is obtained in the form of colourless, transparent prisms which melt at 55°.

* Further experiments show that the yield is to some extent dependent on conditions such as quantity of solvent and duration of heating. This primary yield is in no sense to be regarded as the maximum obtainable; if the residue be well washed, dried, and again subjected to the action of hydrogen chloride, a further yield is obtained which in amount appears to fall not far short of that originally produced.

The substance, after being dried in a vacuum, was analysed with the following results:

0·1473 gave 0·3082 CO_2 and 0·0603 H_2O. C = 57·05; H = 4·54.
$C_8H_8O_4$ requires C = 57·14; H = 4·76 per cent.

Benzoxymethylfurfural, $O{:}CH{\cdot}C_4H_2O{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_6H_5$.—This compound was obtained in a manner similar to that employed in the preparation of the acetoxy-derivative, using silver benzoate, with acetone as solvent in place of acetic acid. After crystallisation from dry ether and from light petroleum, it was obtained in the form of stellate aggregates of long, colourless prisms melting at 56—57°.

0·1188 gave 0·2962 CO_2 and 0·0451 H_2O. C = 67·99; H = 4·22.
$C_{13}H_{10}O_4$ requires C = 67·82; H = 4·34 per cent.

Preparation of 5-Methylfurfural.—Both the bromo- and the chloro-derivatives are easily reduced by stannous chloride in acid solution, giving methylfurfural identical in every respect with that obtained by fractionation of the product of dry distillation of wood, &c., and from rhamnose by the action of dilute acids.

Powdered crystals of the bromo-derivative were covered with excess of a strong solution of freshly prepared stannous chloride in hydrochloric acid and allowed to stand overnight. The mixture was then neutralised with solid sodium carbonate and distilled in steam, when a considerable quantity of nearly colourless oil separated in the distillate. The latter was shaken with ether, and the ethereal solution dried over calcium chloride. After distilling off the ether, the product boiled at 186—187°, and was analysed with the following results:

0·2135 gave 0·5135 CO_2 and 0·1015 H_2O. C = 65·58; H = 5·28.
$C_6H_6O_2$ requires C = 65·45; H = 5·45 per cent.

Fourteen grams of the bromo-derivative gave about 1·9 grams of pure methylfurfural, or about 23 per cent. of that required by theory, and this yield could doubtless be increased by slight modification of the details of preparation.

The reactions of the product are in every way similar to those of the substance prepared in the other ways mentioned. With aniline acetate, it gives at first only a slight yellow colour and this, on standing for some time, changes to a bright orange-red. When a dilute solution of the substance in alcohol is carefully mixed with strong sulphuric acid, an intense and beautiful grass-green colour is developed in the upper layer of liquid (Maquenne's reaction).

The chloro-derivative also readily gives methylfurfural under similar treatment, and the yield appears to be as good or better. For this purpose, it is not necessary first to isolate the chloro-derivative; the

mixture produced by action of hydrogen chloride on the carbohydrate may be mixed directly with excess of stannous chloride and the further operations conducted as before. It is advisable to remove most of the acid as above suggested in order to avoid excessive neutralisation. Bearing in mind the difficulty of obtaining pure methylfurfural by the older methods, it would appear that the process here described offers very considerable advantages.

Difurfurylethanedialdehyde.

When bromomethylfurfural, dissolved in an appropriate solvent, is heated with finely divided metallic silver, the bromine is entirely removed and a beautifully crystalline product results. Other metals in the ordinary state, such as zinc, sodium, or magnesium, appear to have little, if any, action, and in the case of silver the state of division is of great importance. The first experiments were made with silver precipitated by the sulphite method, toluene being used as solvent, and the mixture heated in sealed tubes for several hours to about 140°. Only a very small yield was obtained in this way, and it was afterwards found that by using silver reduced from the chloride by zinc, an energetic action takes place, the whole of the bromine being removed in about half an hour, and a large yield of the product obtained.

The method now adopted is as follows. Recrystallised bromomethylfurfural is mixed with a considerable excess ($1\frac{1}{2}$ to 2 parts by weight) of finely divided silver (prepared by reducing the chloride with zinc, digesting for 24 hours with dilute sulphuric acid, washing successively with water, alcohol, ether, and benzene). The mixture is then covered with two or three times its volume of dry benzene, and heated to boiling in a reflux apparatus on a water-bath until a drop of the liquid gives no reaction with silver nitrate and nitric acid. Considerable heat is evolved in the action, the mixture becoming warm even before external heat is applied, and the operation is completed in about 30—45 minutes.

The solution is filtered off, the residue further extracted three or four times with boiling benzene, and the greater part of the benzene distilled off, when, on cooling, a bulky, yellow precipitate separates. This is drained on a porous plate and recrystallised from a mixture of boiling benzene and light petroleum. Thus obtained, the product is still bright yellow, but it may be further purified by recrystallisation from boiling water, from which it separates on cooling in long, slender prisms which are almost colourless. The substance dissolves easily in cold chloroform and fairly easily in cold glacial acetic acid, but is very sparingly soluble in most other cold solvents. It dissolves easily in hot benzene and sparingly in boiling water. It melts sharply without

decomposition at 119—120°, and at a higher temperature partly vaporises, giving a crystalline sublimate.

A dilute alcoholic solution of the substance when cautiously mixed with concentrated sulphuric acid gives a grass-green colour, resembling in this respect the behaviour of methylfurfural.

The substance, dried at 100°, was analysed with the following results:

0·1168 gave 0·2826 CO_2 and 0·0478 H_2O. C = 65·98; H = 4·54.
0·1253 „ 0·3024 CO_2 „ 0·0483 H_2O. C = 65·82; H = 4·28.
$(C_6H_5O_2)_x$ requires C = 66·05; H = 4·54 per cent.

The molecular weight was determined by the freezing point method using acetic acid as solvent, and the results obtained were remarkably concordant.

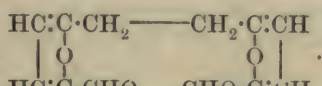
	Solvent.	Solute.	Depression.	Molecular weight.
I.	11·12	0·1974	0·307	224
II.	—	0·4093	0·635	225
III.	13·43	0·2053	0·264	224
IV.	—	0·3307	0·424	225

The calculated molecular weight for $C_{12}H_{10}O_4$ is 218.

The action therefore consists in the removal of two atoms of bromine from two molecules of bromomethylfurfural with linking of the residues.

$$2C_6H_5O_2Br + 2Ag = C_{12}H_{10}O_4 + 2AgBr.$$

From the constitution of bromomethylfurfural which was previously established (Trans., 1899, 75, 429), it follows that the product at present under consideration must be represented by the following formula:



It is difficult to give this substance a simple name; difurfurylethanedialdehyde seems to be the most appropriate.

Action of Phenylhydrazine.—Phenylhydrazine, benzylphenylhydrazine, and hydrazine all give white or buff precipitates with solutions of the above condensation product. A solution of the substance in strong acetic acid was mixed with rather more than twice the molecular proportion of phenylhydrazine as acetate, and the resulting bulky, nearly white precipitate was well washed with acetic acid and then with water. It was then dried in a vacuum desiccator and recrystallised from a cold mixture of absolute alcohol and ether, from which it separated in clusters of minute, transparent plates melting at 179—181°. These, dried in a vacuum desiccator, were analysed with the following result:

0·1501 gave 18·84 c.c. nitrogen at 17° and 747 mm. N = 14·53.
$C_{24}H_{22}O_2N_4$ requires N = 14·07 per cent.

The compound is therefore a *dihydrazone* having the formula $C_{12}H_{10}O_2(N_2H{\cdot}C_6H_5)_2$.

Action of Hydroxylamine.—A warm alcoholic solution of the dialdehyde was mixed with rather more than two molecular proportions of free hydroxylamine, also in alcoholic solution, prepared by Wohl's method. After standing for about 24 hours in a closed flask, the solution was allowed to evaporate in a vacuum desiccator over sulphuric acid, when a white, crystalline substance was deposited. This was washed with cold chloroform and recrystallised from a hot mixture of absolute alcohol and chloroform, from which it separated in colourless prisms melting at 182°. It dissolves fairly easily in warm alcohol, but is very slightly soluble in chloroform or ether. On analysis:

0·1825 gave 17·5 c.c. nitrogen at 16° and 746 mm. N = 11·15.
$C_{12}H_{12}O_4N_2$ requires N = 11·29 per cent.

The substance is therefore a *dioxime* having the formula $C_{12}H_{10}O_2(NOH)_2$.

Difurfurylethanedicarboxylic Acid.

The dialdehyde was oxidised with silver oxide in a manner similar to that employed by Hill and Jennings for the oxidation of methylfurfural (*Amer. Chem. Journ.*, 1893, 15, 167). The substance was mixed with water and an excess of freshly precipitated, well washed silver oxide, and heated in a water-bath to boiling for about half an hour. A slight excess of sodium carbonate was then added, the mixture again boiled for ten minutes, filtered, evaporated to smaller bulk, again filtered, and strongly acidified with hydrochloric acid. A voluminous white or yellowish precipitate was immediately produced, which, after cooling, was collected on a suction filter, well washed with cold water, and recrystallised, first from hot dilute alcohol and then from a mixture of absolute alcohol and toluene. The product is seen under the microscope to consist of minute, transparent prisms. It melts at 267—269°, turning black and decomposing at the same time. It is almost insoluble in cold water, acetic acid, benzene, &c., but dissolves fairly easily in hot alcohol, and easily in alkalis.

For analysis, the acid was dried at 100°:

0·1394 gave 0·2923 CO_2 and 0·0488 H_2O. C = 57·25; H = 3·89.
$C_{12}H_{10}O_6$ requires C = 57·60; H = 4·00 per cent.

The *barium salt* was prepared by dissolving the acid in a considerable excess of hot barium hydroxide solution, removing the excess by carbon

dioxide, boiling, and filtering. On allowing the solution to stand in a desiccator, the salt is slowly deposited in aggregates of transparent plates. For analysis, it was dried at 140°:

0·4813 gave 0·2872 $BaSO_4$. Ba = 35·09.
$C_{12}H_8O_6Ba$ requires Ba = 35·58 per cent.

The barium salt is easily soluble in hot water; its solution is neutral to litmus and gives a white precipitate with silver nitrate or lead acetate.

From the mode of formation and composition of the acid and composition of the barium salt, it is evident that the acid is dibasic and has the constitution:

$$CO_2H\cdot C_4H_2O\cdot CH_2\cdot CH_2\cdot C_4H_2O\cdot CO_2H.$$

When the dry barium salt is mixed with quicklime and strongly heated a yellowish oil distils over and partially crystallises on standing. It is probable that this is the parent substance, difurfurylethane, and the authors intend further to examine it.

Condensation Product with Sulphurous Acid.—It may be observed that the molecular formula for the dialdehyde described above, $C_{12}H_{10}O_4$, differs by CH_2 from that of the product, which the authors previously obtained from the bromo-derivative by the action of sulphurous acid, and proved to have the molecular formula $C_{11}H_8O_4$ (Trans., 1899, 75, 431). Recent experiments with the latter compound indicate that it also reacts with two mols. of phenylhydrazine. The product does not crystallise well, so was analysed after washing carefully and then drying in a vacuum desiccator.

0·2169 gave 27·0 c.c. nitrogen at 19° and 731 mm. N = 14·04.
$C_{23}H_{20}O_2N_4$ requires N = 14·58 per cent.

This phenylhydrazine derivative dissolves in concentrated sulphuric acid with a green colour, which is changed to an intense blue by the addition of manganese dioxide.

At first sight, therefore, it might be thought probable that this condensation product and the dialdehyde were homologous compounds of the same type, but this is probably not the case, since the former gives very remarkable colour reactions, which distinguish it in a marked way from the dialdehyde; with caustic alkalis, it gives an intense blue, and with aniline acetate a brilliant green colour. Further experiments are now being made with this product, and it is found that it may be produced in a similar way by the action of sulphurous acid on the chloro- and on the acetoxy-derivatives. The authors previously suggested that it might be methylfuril, $C_4H_3O\cdot CO\cdot CO\cdot C_4H_2O\cdot CH_3$, and the experiments

made up to the present time are in harmony, either with this assumption, or with the alternative ketone-aldehyde formula,

$$CHO{\cdot}C_4H_2O{\cdot}CO{\cdot}C_4H_2O{\cdot}CH_3.$$

The isolation of the derivatives mentioned in this and preceding communications has suggested a large number of further investigations which the authors hope shortly to undertake. It would be of much interest, if, by a reversal of the change mentioned, a carbohydrate could be regenerated from one of these compounds, for example, from the hydroxy-derivative, and some experiments have already been made in this direction.

The study of the action of hydrogen cyanide on the dialdehyde and of hydrogen iodide on the dicarboxylic acid also promises to give results of considerable interest.

Most of the materials necessary for this research have been obtained by means of funds kindly supplied by the Government Grant Committee of the Royal Society.

LXXXVI.—*The symmetrical Trichlorobromoanilines and Chloro- and Bromo-amino-derivatives of Chlorobromoacetanilides.*

By F. D. Chattaway and K. J. P. Orton.

Of the two symmetrical chlorodibromoanilines, 4-chloro-2 : 6-dibromoaniline was prepared by Hofmann (*Annalen*, 1845, **53**, 38) by brominating *p*-chloroaniline, and 2-chloro-4 : 6-dibromoaniline by Langer (*Annalen*, 1882, **215**, 115) by brominating *o*-chloroaniline. By chlorinating *p*-bromoaniline, Fittig and Büchner (*Annalen*, 1876, **188**, 22) obtained 2 : 6-dichloro-4-bromoaniline. The isomeric 2 : 4-dichloro-6-bromoaniline has hitherto not been described. These anilines have not been well characterised; Hofmann does not give the melting point of the substance prepared by him, and none of the anilides have been described.

The two isomeric anilines not only resemble one another very closely in crystalline form, but possess melting points which lie very near together. The melting points of the anilides also are only two or three degrees apart. Thus, 4-chloro-2 : 6-dibromoaniline and 2-chloro-4 : 6-dibromoaniline melt respectively at 97° and 95°, whilst their acetyl derivatives both melt at 227°. Were it not for the fact that the

acetylchloroamino-derivatives of these anilides have melting points differing by 10 degrees, these anilines would be practically undistinguishable.

The nitrogen chlorides and bromides described in this paper resemble in every way the analogous compounds previously prepared. The methods of preparation are substantially the same as those formerly used, although in some details they have been slightly modified.

4-Chloro-2 : 6-dibromoaniline, $C_6H_2ClBr_2 \cdot NH_2$, is prepared by adding a solution of *p*-chloroaniline in excess of hot glacial acetic acid to the calculated quantity of bromine dissolved in the same solvent. On cooling, practically all the 4-chloro-2 : 6-dibromoaniline separates in almost colourless needles. If excess of bromine is used, the crystals have a faint reddish colour, which can only be removed by distilling once or twice in steam. To completely purify the aniline, it is best to recrystallise it from hot alcohol, when it separates in needles often 3 or 4 cm. in length. In hot alcohol, acetic acid, benzene, chloroform, acetone, or petroleum, it is readily soluble but is only very sparingly so in any cold solvent. It distils easily in steam, melts at 97°, and boils at 301° under 760 mm. pressure. As was to be expected, the salts are very unstable and undergo hydrolysis with water.

0·3175 gave 0·5726 AgCl + AgBr and 0·2168 Cl + Br.* Cl = 12·17 ; Br = 55·85.

$C_6H_4NClBr_2$ requires Cl = 12·42 ; Br = 56·03 per cent.

4-Chloro-2 : 6-dibromoacetanilide, $C_6H_2ClBr_2 \cdot NHAc$.—The aniline is best acetylated, as are all diortho-substituted anilines, by adding a slight excess of acetyl chloride to a hot solution of the base in glacial acetic acid. The anilide crystallises well from glacial acetic acid or alcohol in well developed, often flattened prisms or needles melting at 226—227°. It is insoluble in all solvents and extremely difficult to hydrolyse. Only after many hours' boiling with alcoholic hydrochloric acid is hydrolysis complete.

0·2062 gave 0·3233 AgCl + AgBr and 0·122 Cl + Br ; Cl = 10·47 ; Br = 48·68.

$C_8N_6ONClBr_2$ requires Cl = 10·82 ; Br = 48·87 per cent.

Acetylchloroamino-4-chloro-2 : 6-dibromobenzene, $C_6H_2ClBr_2 \cdot NClAc$, is prepared by slowly adding excess of a concentrated solution of bleaching powder (about normal) to a solution of the corresponding anilide in hot glacial acetic acid. If sufficient acetic acid is used, the chloro-

* To estimate the chlorine and bromine, the mixed silver chloride and bromide obtained in the usual Carius estimation, are weighed in a Gooch crucible, which is then heated in a Rose's crucible, in a current of hydrogen, for twenty minutes. The loss of weight represents the chlorine and bromine.

amino-derivative does not separate as an oil, but crystallises out on cooling in lustrous, white plates. It is thus obtained purer than if allowed to separate in a molten state. It is very soluble in chloroform or benzene, less so in acetic acid, and can readily be recrystallised from petroleum (b. p. 50—80°). It separates from the last solvent in short, four-sided prisms, often resembling cubes, melting at 110—111°.

0·5066 liberated I = 28·02 c.c. *N*/10 iodine. Cl as :NCl = 9·8.
$C_8H_5ONCl_2Br_2$ requires Cl as :NCl = 9·8 per cent.

On heating this compound in a sealed tube with glacial acetic acid at 160° for a short time, decomposition took place with the evolution of a small quantity of bromine. The only substance which could be isolated was the original anilide, 4-chloro-2 : 6-dibromoacetanilide, which was formed by hydrolysis from the nitrogen chloride. The anilide is most easily recognised by recrystallising from acetic acid the product obtained after heating in the sealed tube, and then converting it into the chloroamino-derivative. Not only is the latter very quickly analysed, but the melting point is far removed from the melting points of the chloroamino-derivatives of either of the two symmetrical dichlorobromoacetanilides, which might be formed by replacement of bromine by chlorine.

2-*Chloro*-4 : 6-*dibromoaniline*, $C_6H_2ClBr_2{\cdot}NH_2$, was obtained by Langer (*loc. cit.*) by the action of excess of bromine water on an aqueous solution of *o*-chloroaniline hydrochloride. It is more convenient to prepare this compound by brominating *o*-chloroaniline (obtained from carefully purified *o*-chloroacetanilide) in the manner above described. We have also prepared it by brominating 2-chloro-4-bromoaniline. Langer gives the melting point of the aniline as 95°; the compound obtained by us in either way melted exactly at this temperature.

2-*Chloro*-4 : 6-*dibromoacetanilide*, $C_6H_2ClBr_2{\cdot}NHAc$, was prepared as described above. It forms flattened prisms or needles melting at 227°, and is practically indistinguishable from the isomeric 4-chloro-2 : 6-dibromoacetanilide.

0·1129 gave 0·1787 AgCl + AgBr and 0·0674 Cl + Br. Cl = 10·62; Br = 49·09.
$C_8H_6ONClBr_2$ requires Cl = 10·82; Br = 48·87 per cent.

Acetylchloroamino-2-*chloro*-4 : 6-*dibromobenzene*, $C_6H_2ClBr_2{\cdot}NClAc$, prepared from the anilide as above described, crystallises from petroleum in four-sided prisms and from dilute acetic acid containing hypochlorous acid in plates melting at 99—100°.

0·2322 liberated I = 12·98 c.c. *N*/10 iodine. Cl as :NCl = 9·9.
$C_8H_7ONCl_2Br_2$ requires Cl as :NCl = 9·8 per cent.

On heating for a short time at 160° with acetic acid in a sealed tube, decomposition takes place, with evolution of a small amount of bromine. The chief product is re-formed 2-chloro-4 : 6-dibromoacetanilide.

2 : 6-*Dichloro*-4-*bromoaniline*, $C_6H_2Cl_2Br\cdot NH_2$.—Fittig and Büchner (*loc. cit.*) obtained this aniline, together with 2-chloro-4-bromoaniline, by chlorinating a hot aqueous solution of *p*-bromoaniline hydrochloride. We find the following method gives a better yield than theirs, and is more convenient. A cold solution of *p*-bromoaniline in chloroform is slowly added in small portions at a time to well cooled chloroform saturated with dry chlorine. After each addition of the base, chlorine gas is again passed in. During the process, the hydrochloride of 2 : 6-dichloro-4-bromoaniline is precipitated. This is filtered off and decomposed by dilute aqueous ammonia; the aniline thus obtained is recrystallised from alcohol, from which solvent it separates in long needles melting at 92° (Fittig and Büchner give 93·5°). It is more soluble in cold solvents than the chlorodibromoanilines.

2 : 6-*Dichloro*-4-*bromoacetanilide*, $C_6H_2Cl_2Br\cdot NHAc$, forms flattened prisms or needles melting at 214°.

0·3162 gave 0·5279 AgCl + AgBr and 0·1677 Cl + Br. Cl = 24·93; Br = 28·11.

$C_8H_6ONCl_2Br$ requires Cl = 25·06; Br = 28·26 per cent.

Acetylchloroamino-2 : 6-*dichloro*-4-*bromobenzene*, $C_6H_2Cl_2Br\cdot NClAc$, crystallises in plates from dilute acetic acid containing hypochlorous acid, and from petroleum in prisms melting at 81°.

0·2349 liberated I = 14·72 c.c. *N*/10 iodine. Cl as :NCl = 11·11.

$C_8H_5ONCl_3Br$ requires Cl as :NCl = 11·17 per cent.

2 : 4-*Dichloro*-6-*bromoaniline*, $C_6H_2Cl_2Br\cdot NH_2$, is readily prepared by brominating 2 : 4-dichloroaniline. It is very soluble in benzene or chloroform, and fairly so in petroleum or dilute alcohol. It crystallises in long, white, lustrous needles melting at 83·5° and boiling at about 273° under the ordinary atmospheric pressure.

0·2324 gave 0·4578 AgCl + AgBr and 0·1454 Cl + Br. Cl = 29·48; Br = 33·09.

$C_6H_4NCl_2Br$ requires Cl = 29·43; Br = 33·18 per cent.

2 : 4-*Dichloro*-6-*bromoacetanilide*, $C_6H_2Cl_2Br\cdot NHAc$, forms flattened prisms or needles melting at 218°.

0·2257 gave 0·377 AgCl + AgBr and 0·1202 Cl + Br. Cl = 24·71; Br = 28·53.

$C_8H_6ONCl_2Br$ requires Cl = 25·06; Br = 28·26 per cent.

Acetylchloroamino-2 : 4-*dichloro*-6-*bromobenzene*, $C_6H_2Cl_2Br\cdot NClAc$, crystallises from petroleum in four-sided prisms, melting at 91—92°.

0·2288 liberated I = 14·4 c.c. *N*/10 iodine. Cl as :NCl = 11·15.
$C_8H_5ONCl_3Br$ requires Cl as :NCl = 11·17 per cent.

2 : 6-*Dibromoacetanilide*, $C_6H_3Br_2\cdot NHAc$, obtained as above from the aniline, crystallises from alcohol, in which it is moderately soluble, in white prisms melting at 208—209°.

0·2233 gave 0·2856 AgBr. Br = 54·42.
$C_8H_7ONBr_2$ requires Br = 54·58 per cent.

Acetylchloroamino-2 : 6-*dibromobenzene*, $C_6H_3Br_2\cdot NClAc$, crystallises from petroleum in small prisms melting at 88°.

0·3198 liberated I = 10·0 c.c. *N*/10 iodine. Cl as :NCl = 11·07.
$C_8H_6ONClBr_2$ requires Cl as :NCl = 10·82 per cent.

Although many attempts were made to transform this nitrogen chloride into the isomeric 4-chloro-2 : 6-dibromoacetanilide, under no circumstances could the chlorine be induced to pass from the nitrogen atom to the para-position in the benzene ring. The nitrogen chloride was found to undergo change only when it was heated in a sealed tube for some time with glacial acetic acid at 140—150°. The product then contained no nitrogen chloride. In order to determine whether any isomeric change had occurred, it was boiled with alcohol and sulphuric acid to convert the anilide into aniline, and then distilled in steam. The substance which separated from the distillate melted at 84°, the melting point of 2 : 6-dibromoaniline, and gave an anilide melting at 207°. The latter yielded a chloroamino-derivative melting at 88°, which on analysis was found to contain Cl as :NCl = 10·85 per cent. No transformation had, therefore, taken place; the chloroamino-derivative had simply hydrolysed on heating with acetic acid.

Acetylbromoamino-4-*chlorobenzene*, $C_6H_4Cl\cdot NBrAc$.—This substance was prepared in the usual manner (Chattaway and Orton, *Ber.*, 1899, **32**, 3573). When crystallised from a mixture of chloroform and petroleum, it forms yellow, four-sided plates melting at 91°.

0·2529 liberated I = 20·3 c.c. *N*/10 iodine. Br as :NBr = 32·09.
$C_8H_7ONClBr$ requires Br as :NBr = 32·17 per cent.

It is transformed quantitatively into the isomeric 4-chloro-2-bromoacetanilide (m. p. 137°) on allowing a solution in a mixture of chloroform and acetic acid to stand for 12 hours.

Acetylchloroamino-4-*bromobenzene*, $C_6H_4Br\cdot NClAc$, was prepared by shaking up finely-powdered *p*-bromoacetanilide with a slight excess of bleaching powder solution just acidified with acetic acid. Chloroform was added to dissolve the nitrogen chloride. After evaporation of

the solvent, the substance was recrystallised from petroleum, from which it separates in large, white rhombs melting at 108—109°.

0·2631 liberated I = 20·9 c.c. *N*/10 iodine. Cl as :NCl = 14·15.
$C_8H_7ONClBr$ requires Cl as :NCl = 14·26 per cent.

In a solution in acetic acid, or in a mixture of acetic acid and chloroform, it is transformed quantitatively into 2-chloro-4-bromoacetanilide (m. p. 151°).

Acetylbromoamino-2 : 4-*dichlorobenzene*, $C_6H_3Cl_2{\cdot}NBrAc$, crystallises from a mixture of chloroform and petroleum in lustrous, yellow plates or prisms melting at 95—96°.

0·2453 liberated I = 17·28 c.c. *N*/10 iodine. Br as :NBr = 28·16.
$C_8H_6ONCl_2Br$ requires Br as :NBr = 28·26 per cent.

It is transformed into the isomeric 2 : 4-dichloro-6-bromoacetanilide when carefully heated alone at 130° for some 45 minutes.

Acetylchloroamino-4-*chloro*-2-*bromobenzene*, $C_6H_3ClBr{\cdot}NClAc$, was prepared by adding a solution of bleaching powder to a solution of 4-chloro-2-bromoacetanilide in glacial acetic acid. It crystallises from petroleum in four-sided prisms melting at 74—75°.

0·2533 liberated I = 18·04 c.c. *N*/10 iodine. Cl as :NCl = 12·63.
$C_8H_6ONCl_2Br$ requires Cl as :NCl = 12·53 per cent.

On heating in a sealed tube with acetic acid up to 150°, it is partially transformed into 2 : 4-dichloro-6-bromoacetanilide, and partially hydrolysed, re-forming 4-chloro-2-bromoacetanilide.

Acetylbromoamino-4-*chloro*-2-*bromobenzene*, $C_6H_3ClBr{\cdot}NBrAc$ forms yellow rhombs melting at 85—86°.

0·218 liberated I = 13·4 c.c. *N*/10 iodine. Br as :NBr = 24·57.
$C_8H_6ONClBr_2$ requires Br as :NBr = 24·64 per cent.

On heating alone at 130° for a short time, it changes into the isomeric 4-chloro- 2 : 6-dibromoacetanilide melting at 227°.

Acetylchloroamino-2-*chloro*-4-*bromobenzene*, $C_6H_3ClBr{\cdot}NClAc$, crystallises in rhombs or four-sided prisms melting at 88—89°.

0·2693 liberated I = 19·15 c.c. *N*/10 iodine. Cl as :NCl = 12·6.
$C_8H_6ONCl_2Br$ requires Cl as :NCl = 12·53 per cent.

On heating in a sealed tube with acetic acid to 140°, transformation takes place. The product crystallises in fine prisms, which gave correct numbers for a dichlorobromoacetanilide; but the melting point cannot be raised above 205°, whereas pure 2 : 6-dichloro-4-bromoacetanilide melts at 214°. This is probably due to a partial displacement of the bromine from the para-position during the transformation.

Acetylbromoamino-2-*chloro*-4-*bromobenzene*, $C_6H_3ClBr{\cdot}NBrAc$, forms

brilliant, four-sided, yellow prisms, often nearly cubical, melting at 110—111°.

0·257 liberated I = 7·9 c.c. *N*/10 iodine. Br as :NBr = 24·58.
$C_8H_6ONClBr_2$ requires Br as :NBr = 24·44 per cent.

On heating for a short time at 130°, it is transformed into the isomeric 2-chloro-4 : 6-dibromoacetanilide.

Acetylchloroamino-2 : 4-*dibromobenzene*, $C_6H_3Br_2{\cdot}NClAc$, forms lustrous, white plates or rhombs melting at 56—57°.

0·3652 liberated I = 22·18 c.c. *N*/10 iodine. Cl as :NCl = 10·76.
$C_8H_6ONClBr_2$ requires Cl as :NCl = 10·82 per cent.

This nitrogen chloride is readily transformed when heated at 100° for 1 hour with acetic acid in a sealed tube. The product gives correct numbers for a chlorodibromoacetanilide, but the melting point cannot be raised above 221°. It is probable that the product of this transformation is a mixture of the two chlorodibromoacetanilides, partial displacement of the bromine having taken place.

Acetylchloroamino-2 : 4 : 6-*tribromobenzene*, $C_6H_2Br_3{\cdot}NClAc$, forms highly refractive crystals melting at 109—110°.

0·2795 liberated I = 13·4 c.c. *N*/10 iodine. Cl as :NCl = 8·5.
$C_8H_5ONClBr_3$ requires Br as :NBr = 8·72 per cent.

When heated in a sealed tube with acetic acid at 160°, this substance decomposes with evolution of bromine. The product, after repeated recrystallisation, melts at 220° and contains 4 per cent. of chlorine. It was converted into the nitrogen chloride, which, after repeated recrystallisation from petroleum, melted at 109°, and contained Cl as :NCl = 8·5 per cent. From the purified nitrogen chloride, *s*-tribromoacetanilide melting at 232° was obtained.

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LXXXVII.—*The Replacement of Bromine by Chlorine in Anilines.*

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THE replacement of one halogen by another in anilines was first observed by Wegscheider (*Monatsh.*, 1897, 18, 329). On heating *s*-tribromoaniline with hydrochloric acid at 240°, he obtained nearly pure *s*-trichloroaniline. When *s*-trichloroaniline was heated with

hydrobromic acid, bromine replaced chlorine to some extent, and apparently mixtures of chlorobromoanilines were produced.

About the same time, Hantzsch (*Ber.*, 1897, 30, 2334) showed that bromobenzenediazonium chlorides are transformed under certain conditions into chlorobenzenediazonium bromides, but that the reverse changes never take place. This interchange of bromine and chlorine only occurs when the bromine atoms occupy ortho- and para-positions relatively to the diazonium group. Hantzsch and Smythe (*Ber.*, 1900, 33, 505) further find that the velocity of the reaction in certain dibromo-compounds is greater when both bromine atoms occupy ortho-positions than it is when one bromine atom is in the ortho- and the other in the para-position. From this he concludes that the interchange between the chlorine atom attached to the nitrogen and the bromine atom attached to the nucleus takes place more readily when the bromine atom occupies an ortho-position relatively to the diazonium group. From among the products of the reaction, Hantzsch never isolated any compound in which chlorine had replaced bromine in the ortho- and not in the para-position, nor did he show that the chlorobromo-compound he obtained from 2:4-dibromobenzenediazonium chloride possessed the orientation $N_2 : Cl : Br = 1 : 2 : 4$, and not $N_2 : Br : Cl = 1 : 2 : 4$.

In the course of our work on the chloroamino-derivatives of bromoanilides, it was observed that bromine was evolved when acylchloroaminobromobenzenes, in which bromine occupied an ortho- or para-position relatively to the nitrogen, were heated with acetic acid in a sealed tube. This evolution was very obvious with derivatives of *s*-tribromoaniline, and to a less extent with those of *s*-chlorobromoanilines. Very little replacement of bromine by chlorine, however, takes place under these conditions, the chloroamino-derivatives mainly suffering hydrolysis, with regeneration of the anilide. It was found impossible to separate from the large quantity of anilide regenerated the small amount of material in which chlorine had partly replaced the bromine.

On treating *s*-tribromoaniline, however, with an acetylchloroamino-derivative, the evolution of bromine is very marked; and beside azo-compounds* (compare this vol., 461) and colouring matters soluble in alcohol, a chlorodibromoaniline can be isolated. To investigate this reaction further, we prepared the two *s*-chlorodibromoanilines and the two *s*-dichlorobromoanilines, and studied their behaviour with chloroamino-derivatives.

When molecular proportions of acetylchloroamino-2:4-dichloro-

* The azo-compound, although it crystallised well, was found, with this and with the other anilines investigated, to be a mixture of which the separation was impracticable.

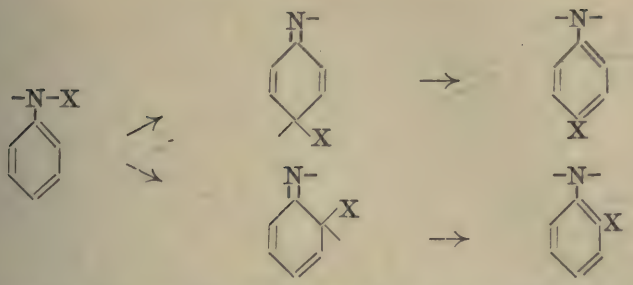
benzene and one or other of the above anilines were mixed in chloroform solution, it was at once noticeable that those anilines which possessed a bromine atom in the para-position gave off bromine at the ordinary temperature to a far greater extent than those in which bromine was in the ortho-positions only. Thus, 2-chloro-4:6-dibromoaniline gave off a considerable quantity of bromine, whilst the isomeric 4-chloro-2 : 6-dibromoaniline evolved very little. Further, whilst in the case of the latter aniline no dichlorobromo-derivative could be obtained, from the former a dichlorobromoaniline was isolated. The same holds for the two *s*-dichlorobromoanilines. From 2:6-dichloro-4-bromoaniline much bromine was evolved and *s*-trichloroaniline obtained, whilst little bromine was given off from 2 : 4-dichloro-6-bromoaniline and sufficient *s*-trichloroaniline was not formed to allow us to isolate it.

By means of the chloroamino-derivatives of the anilides (this vol., 816), we have been able to prove that the chlorodibromoaniline obtained, from *s*-tribromoaniline has the chlorine atom in the para-position, and that 2-chloro-4 : 6 dibromoaniline yields 2 : 4-dichloro-6-bromoaniline. In both cases, it is the bromine atom in the para-position which is chiefly replaced by chlorine.

We have every reason to believe (this vol., 461) that in the reaction between acylchloroamino-derivatives and anilines there is first formed a chloroamino-derivative of the aniline, which then undergoes the usual isomeric change, producing a para- or ortho-substituted aniline; the chlorine in this case exchanges positions with the hydrogen. In the case under consideration, instead of a replaceable hydrogen atom, there is a replaceable bromine atom, which is, however, much less mobile than the hydrogen.

The above experiments, as well as all our observations on the transformation of acylchloroamino- and acylbromoamino-benzenes, clearly demonstrate the readiness with which the halogen attached to the nitrogen atom is transferred to the para-carbon atom of the benzene ring. Whatever the intermediate configurations (if any) through which a chloro- or bromo-amino-derivative passes during the isomeric change, it is certain that those which lead to the formation of para-compounds are assumed more readily than those which lead to the formation of ortho-compounds.

For a considerable time it has appeared to us probable that an iminoquinone is the intermediate stage, and quite recently Bamberger (*Ber.*, 1900, **33**, 3600; 1901, **34**, 61) has shown that in all probability an imino-ψ-quinol is an intermediate stage in the transformation of β-phenylhydroxylamine into *p*-aminophenol. On this view, the transformation of a halogen amino-derivative may be represented thus:



Of the *p*- and *o*-quinone forms, which have alone been observed, the former seems to be the one which the benzene nucleus most readily takes up. The chloroamino-derivative, in assuming an iminoquinone form, would then be more likely to change into a *p*-iminoquinone than into an *o*-aminoquinone, and consequently the para-atom would be preferentially replaced by chlorine. Various substituting groups attached to the benzene nucleus or different acyl groups attached to the nitrogen might be expected, on this view, to modify the proportion of *o*- and *p*-derivatives formed; this we have repeatedly shown to be the case.

It is seen that, by the above method of representing the change, the formation of the *o*- and *p*-derivatives are not successive stages of the same process, but are initially different.*

We have not so far isolated any substance which might be the intermediate product or the derivative of an intermediate product, and must leave unanswered the question, How is the quinone form produced from the halogen amino-derivative. In the case of the phenylhydroxyl amines, Bamberger thinks that a decomposition of the hydroxylamine into the elements of water and a residue $C_6H_5 \cdot N <$ precedes the formation of the ψ-quinol. The observations of Hantzsch (*loc. cit.*) seem to show that the interchange of chlorine for bromine in bromobenzenediazonium chlorides is an intramolecular change and that ionisation of the salt does not facilitate but prevents it.

Experimental.

Reaction of Acetylchloroamino-2 : 4-dichlorobenzene with s-Tribromoaniline and s-Trichlorobromoanilines.

s-Tribromoaniline.—Equivalent quantities of acetylchloroamino-2 : 4-dichlorobenzene and *s*-tribromoaniline were mixed in dry chloroform, and the solution was allowed to stand in a stoppered bottle. In the course of 12 hours it became deep red in colour, and smelt strongly of bromine, and 2 : 4-dichloroacetanilide had crystallised out. After

* We know of no instance of the transformation of an *o*-chloro- or *o*-bromoaniline into a *p*-compound.

filtering off the crystals, the chloroform was evaporated, and the residue dissolved in petroleum in order to remove the remainder of the anilide, which is thus left undissolved. The petroleum was next evaporated, and the residue extracted with boiling alcohol. The azo-derivatives remain undissolved, whilst all the aniline and a colouring matter which we have not yet isolated in a pure state go into solution. The aniline was obtained free from this colouring matter by distilling in steam. It represented about 20 per cent. of the *s*-tribromoaniline used, and melted at 97°. In order to prove its constitution, it was acetylated, and the anilide converted into the chloroamino-derivative, which melted at 110—111°.

0·2273 gave 0·4116 AgCl + AgBr and 0·1555 Cl + Br. Cl = 11·99; Br = 56·41.

$C_6H_4NClBr_2$ requires Cl = 12·42; Br = 56·03 per cent.

0·2777 liberated I = 15·1 c.c. *N*/10 iodine. Cl as :NCl = 9·64.

$C_8H_5ONCl_2Br_2$ requires Cl as :NCl = 9·8 per cent.

Acetylchloroamino-2-chloro-4 : 6-dibromobenzene melts at 99—100°, whilst acetylchloroamino-4-chloro-2 : 6-dibromobenzene melts at 110—111°. The aniline obtained from *s*-tribromoaniline is then 4-chloro-2 : 6-dibromoaniline.*

4-*Chloro*-2 : 6-*dibromoaniline* was treated in exactly the same way with a nitrogen chloride. Very little bromine was evolved, and the small quantity of aniline isolated from the products of the reaction was chiefly unchanged 4-chloro-2 : 6-dibromoaniline. Thus it melted at 94° (pure 4-chloro-2 : 6-dibromoaniline melts at 97°), and the anilide yielded a chloroamino-derivative melting at 106°, and containing Cl as :NCl = 10·2 per cent., whilst the pure chloroamino-derivative of this anilide melts at 110—111° and contains Cl as :NCl = 9·8 per cent. Acetylchloroamino-2 : 4-dichloro-6-bromobenzene melts at 91—92°, and contains Cl as :NCl = 11·17 per cent.

A quantitative comparison of the amounts of bromine given off in the reaction of acetylchloroamino-2:4-dichlorobenzene with *s*-tribromoaniline and 4-chloro-2 : 6-dibromoaniline respectively, showed very clearly the far greater liberation of bromine from the para-position than from the two ortho-positions.

One gram of the nitrogen chloride (1 mol.) was mixed in chloroform solution with 1·5 grams of *s*-tribromoaniline (1·4 mols.). After stand-

* Using very carefully dried material, we have noticed, on one or two occasions, less liberation of bromine. On evaporating the solution, we once obtained a solid substance which decomposed rapidly with evolution of bromine. In every other case, this decomposition took place during the evaporation of the chloroform. This substance did not appear to be a nitrogen chloride or nitrogen bromide, and may possibly have been the isomeric quinoneimine.

ing for 12 hours, the bromine was driven off by a current of dry carbon dioxide into a solution of potassium iodide. The iodine set free was equivalent to 13·5 c.c. $N/10$ iodine. In an exactly similar experiment, in which 4-chloro-2 : 6-dibromoaniline was used, bromine equivalent to 0·8 c.c. $N/10$ iodine only was evolved.

2-Chloro-4 : 6-dibromoaniline reacted with the nitrogen chloride with marked evolution of bromine. The aniline which separated from the product proved to be chiefly 2 : 4-dichloro-6-bromoaniline. It melted at 81° (instead of at 83°), and the anilide gave a chloroamino-derivative which melted at 89° (instead of at 91—92°), and contained Cl as $:NCl = 11·33$ per cent. (instead of 11·17 per cent.). The isomeric 2 : 6-dichloro-4-bromoaniline melts at 93°, and the chloroamino-derivative of the anilide at 80°.

Similar experiments were made with the two *s*-dichlorobromoanilines. With 2 : 4-dichloro-6-bromoaniline, very little bromine was evolved, and the aniline isolated was unchanged 2 : 4-dichloro-6-bromoaniline (m. p. 83°). When 2 : 6-dichloro-4-bromoaniline was used, much bromine was evolved, and the aniline isolated from the product of the reaction yielded an anilide which melted at 206°. The chloroamino-derivative of the latter melted at 81°, and contained Cl as $:NCl = 12·6$ per cent. These data show that the base isolated was *s*-trichloroaniline, which melts at 77°, whilst the anilide melts at 206°; acetylchloroamino-2 : 4 : 6-trichlorobenzene melts at 80°, and contains Cl as $:NCl = 12·99$ per cent.*

Finally, when 2 : 6-dibromoaniline reacts with a nitrogen chloride, 4-chloro-2 : 6-dibromoaniline is rapidly formed, no bromine being evolved. 2 : 4-Dibromoaniline similarly yields 2-chloro-4 : 6-dibromoaniline, but a slight evolution of bromine takes place. As has already been mentioned (this vol., 461), when by the action of a nitrogen chloride on an aniline, chlorine replaces hydrogen, either in the para- or ortho-position, the reaction proceeds with considerable rapidity. The replacement of bromine by chlorine is a much slower process. Consequently, if a replaceable hydrogen is present (that is, a hydrogen atom in positions 2, 4, or 6), it is always preferentially replaced by the chlorine. Again, the slowness with which the replacement of bromine by chlorine takes place gives an opportunity for other reactions (azo-formation, &c.) to occur. The yield, therefore, of aniline containing more chlorine and less bromine is always small.

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* The melting point was previously given by us as 74°, but this appears to be too low. The melting point of most carefully purified material is about 80°.

LXXXVIII.—*Optically Active Nitrogen Compounds and their Bearing on the Valency of Nitrogen.* d- *and* l-*α-Benzylphenylallylmethylammonium Salts.*

By William Jackson Pope and Alfred William Harvey.

The first rigid proof of the existence of enantiomorphously related isomerides of quaternary ammonium compounds was given (Pope and Peachey, Trans., 1899, 75, 1127) in the case of α-benzylphenylallylmethylammonium salts, and since these compounds still afford the only unquestionable instance of the existence of asymmetric optically active nitrogen derivatives, it seemed desirable to continue their study.

Resolution of α-Benzylphenylallylmethylammonium Iodide.

The method which we now use for the resolution of Wedekind's externally compensated α-benzylphenylallylmethylammonium iodide differs somewhat from that originally given (*loc. cit.*). The quaternary iodide is boiled with one molecular proportion of silver *d*-camphorsulphonate in a nearly dry mixture of acetone and ethyl acetate until interaction is complete, the silver iodide is then separated and the solvent distilled off; the residue, which is at first very gummy, only slowly becomes crystalline. It is convenient to allow the residue to become partly crystalline, and then to macerate it with anhydrous ethyl acetate and filter. The crystalline product consists almost wholly of *d*-benzylphenylallylmethylammonium *d*-camphorsulphonate, and the mother liquors and washings, on evaporation, yield a further quantity of the same salt; ultimately, however, a syrupy residue containing *l*-benzylphenylallylmethylammonium *d*-camphorsulphonate is obtained, the further working up of which, by the method given by Pope and Peachey, offers considerable difficulties. It is convenient to dissolve the syrup in water, add to it the proper proportion of potassium iodide to precipitate all the base as the crystalline iodide, and, after drying this crude *l*-iodide, to digest it with one molecular proportion of silver *l*-camphorsulphonate (Pope and Harvey, this vol., 80), repeating the whole process of crystallisation in the manner described. The major portion of the externally compensated iodide is thus ultimately obtained in the form of the enantiomorphously related salts, *d*-benzylphenylallylmethylammonium *d*-camphorsulphonate and *l*-benzylphenylallylmethylammonium *l*-camphorsulphonate.

d-*Benzylphenylallylmethylammonium* d-*Camphorsulphonate*, $C_6H_5\cdot CH_2\cdot N(C_6H_5)(C_3H_5)(CH_3)\cdot O\cdot SO_2\cdot C_{10}H_{15}O$.

The crude crystalline salt is readily purified by recrystallisation from ethyl acetate, and has the general properties previously described; the carefully purified material melts at 171—173°, instead of at 169—170° as originally stated. In order definitely to establish the rotation constants, a highly purified sample of the salt was crystallised three times from ethyl acetate, and the rotatory powers of the three specimens, *a*, *b*, and *c*, determined in aqueous solution, with the following results:

a. 0·2065 gram, made up to 25·0 c.c. with water at 14°, gave α_D +0·77° in a 2 dcm. tube; whence $[\alpha]_D$ +46·6° and $[M]_D$ +218·6°.

b. 0·2100 gram, made up to 25·1 c.c. with water at 14°, gave α_D +0·78° in a 2 dcm. tube; whence $[\alpha]_D$ +46·6° and $[M]_D$ +218·6°.

c. 0·2116 gram, made up to 25·1 c.c. with water at 14°, gave α_D +0·78° in a 2 dcm. tube; whence $[\alpha]_D$ +46·2° and $[M]_D$ +217·0°.

The practical identity of the numbers for the three fractions indicates the purity of the salt, which thus has the mean molecular rotatory power $[M]_D$ +218·1° in an aqueous solution containing one-fifth gram-molecule per litre; accepting the value $[M]_D$ +51·7° given by Pope and Peachey (Trans., 1899, 75, 1086) for the molecular rotatory power of the *d*-camphorsulphonic ion, that of the *d*-benzylphenylallylmethylammonium ion is obtained as $[M]_D$ +166·4°, a value which compares well with the original one of 'about 150°.'

The aqueous solution of this salt becomes turbid on warming, owing to hydrolytic decomposition, but no change in rotatory power is observed on allowing the aqueous solution, prepared in the cold, to remain at the ordinary laboratory temperature for 10 days.

l-*Benzylphenylallylmethylammonium* l-*Camphorsulphonate*.

The method of purification and the general properties of this salt, which is now described for the first time, are similar to those of its enantiomorphously related isomeride; it melts at 171—173°. On crystallising a highly purified sample three times from ethyl acetate, however, and determining the rotatory powers of the three specimens, *a*, *b*, and *c*, an appreciable difference was observed:

a. 0·3009 gram, made up to 25·1 c.c. with water at 16°, gave α_D −1·09° in a 2 dcm. tube; whence $[\alpha]_D$ −45·5° and $[M]_D$ −213·2°.

b. 0·3100 gram, made up to 25·1 c.c. with water at 16°, gave α_D −1·10° in a 2 dcm. tube; whence $[\alpha]_D$ −44·5° and $[M]_D$ −208·8°.

c. 0·3132 gram, made up to 25·1 c.c. with water at 17°, gave α_D −1·12° in a 2 dcm. tube; whence $[\alpha]_D$ −44·9° and $[M]_D$ −210·5°.

Thus, in an aqueous solution containing one-fourth gram-molecule per litre, the mean molecular rotatory power of the salt is $[M]_D$ −210·8°, a value which is not numerically identical, within the limits of experimental error, with that obtained for the enantiomorphously related isomeride. The difference is remarkable in view of the ease with which the two salts are purified and the fact that the rotatory powers are not sensibly changed by recrystallisation; it cannot be attributed to admixture of the *l*-camphorsulphonate with its optical antipodes, because the sample of acid used was that which previously gave (this vol., 80) the molecular rotatory power $[M]_D$ −51·6° for the *l*-camphorsulphonic ion. The quantity of salt at our disposal was insufficient to permit of the further investigation of this anomaly. The molecular rotatory power of the *l*-benzylphenylallylmethylammonium ion deduced from these numbers is $[M]_D$ −159°.

d-*Benzylphenylallylmethylammonium Iodide*, $C_6H_5{\cdot}CH_2{\cdot}N(C_6H_5)(C_3H_5)(CH_3)I$.

On adding an aqueous solution of one molecular proportion of potassium iodide to a cold aqueous solution of the pure *d*-benzylphenylallylmethylammonium *d*-camphorsulphonate, a colourless, crystalline precipitate of *d*-benzylphenylallylmethylammonium iodide soon begins to separate; it is purified by crystallising several times as rapidly as possible from boiling absolute alcohol, and then forms glistening, diamond-shaped plates which melt and decompose at 147°. The crystallisation from alcohol is best performed by gaslight, because if bright sunlight is allowed to fall on the cooling solution, decomposition takes place, and only a gummy mass is subsequently separable from the solution. In one case, in which a sample of iodide having the specific rotatory power $[\alpha]_D$ +52·3° in cold chloroform was crystallised from alcohol in sunlight, a small quantity of crystalline iodide was ultimately recovered, and this was found to have the specific rotatory power $[\alpha]_D$ +43·6° in cold chloroform solution. Optical inversion, therefore, seems to accompany the decomposition induced by sunlight.

This salt is so sparingly soluble in most media that Pope and Peachey did not find a single solvent in which the substance is sufficiently soluble, without decomposition, to allow of its rotatory power being determined; the values which they obtained from solutions in a mixture of acetone and methyl alcohol are, therefore, of no standard value. The salt dissolves freely and without undergoing decomposition, however, in cold chloroform which has been very carefully purified and preserved in the dark. The following determinations were made with two successive crystallisations, *a* and *b*, from absolute alcohol of a sample which had previously been several times similarly recrystallised:

a. 0·2648 gram, made up to 25·1 c.c. with cold chloroform at 17°, gave α_D +1·17° in a 2 dcm. tube; whence $[\alpha]_D$ +55·4°.

b. 0·2520 gram, made up to 25·0 c.c. with cold chloroform at 17°, gave α_D +1·11° in a 2 dcm. tube; whence $[\alpha]_D$ +55·0°.

In a 1 per cent. solution in cold chloroform, the mean specific rotatory power is therefore $[\alpha]_D$ +55·2°.

If the solution of the salt be hastened by heating in contact with chloroform, the rotatory power decreases very rapidly, and if the warming be continued for more than a few minutes, the solution becomes optically inactive. Further, the fresh chloroform solution, prepared and preserved in the cold, gradually loses its rotatory power; no appreciable loss in rotatory power occurs during the first hour, so that the above determinations may be taken as giving reliable values; the solutions, preserved at the ordinary winter laboratory temperature in the dark and in the absence of air, become quite inactive within three days. The change here involved is, however, very different from that which takes place in the hot alcoholic solution exposed to sunlight, for in that case decomposition of the salt occurs as the principal change, although accompanied by partial inversion of the part which escapes decomposition. That no appreciable decomposition takes place on preserving or warming the chloroform solutions is shown by the fact that, on evaporation to dryness, they yield a crystalline residue showing no trace of gumminess; since this residue has the melting point and other properties of the externally compensated iodide, the action of the chloroform is wholly one of inversion. The optically active iodide, therefore, behaves towards solvents in at least the following three ways:

a. When dissolved in cold chloroform, it gradually undergoes inversion, but without suffering any obvious decomposition, and as, in this case, no question of tautomerism can arise, such as we showed to be the probable cause of the inversion of tetrahydro-β-naphthylamine (this vol., 74), it is difficult to attribute this inversion to any cause but dissociation; as benzyl iodide is produced when the salt is decomposed by hydrolytic agents, the dissociation would naturally be represented by the following equation:

$$C_6H_5\cdot CH_2\cdot N(C_6H_5)(C_3H_5)(CH_3)I \rightleftarrows N(C_6H_5)(C_3H_5)\cdot CH_3 + C_6H_5\cdot CH_2I.$$

This is in accordance with Wedekind's observation (*Stereochemie des fünfwerthigen Stickstoffes, Leipzig*, 1899, 45), that α-benzylphenylallylmethylammonium iodide can be prepared by the combination of allylmethylaniline and benzyl iodide.

b. The salt undergoes decomposition into allylmethylaniline and benzyl iodide in hot alcoholic solution under the influence of sunlight;

slight inversion accompanies the decomposition, that is to say, there is some tendency towards reversal of the decomposition.

c. The salt undergoes no appreciable dissociation or decomposition, as when rapidly crystallised from hot alcohol in absence of sunlight.

The view has been advanced by Le Bel (*Notice sur les travaux de M. Le Bel, Paris*, 1897; *Supplement*, 1899), and supported by others, that, in substituted ammonium compounds, intramolecular vibration of the atomic groups attached to the nitrogen atom may lead to their interchange and, consequently, to the inversion of an optically active ammonium derivative. This is supported by Le Bel's statement that the feebly lævorotatory *iso*butylpropylethylmethylammonium chloride undergoes inversion during conversion into sulphate, mercurichloride, aurichloride, or platinichloride, or by the action of hydrochloric acid. As the very scanty experimental data do not allow us to distinguish whether the occurrence of inactivity is due (1) to decomposition into tertiary base, (2) to dissociation, or (3) to permutation between the atomic groups, little reason exists for accepting Le Bel's conclusion (*Compt. rend.*, 1900, 130, 1552) that such inversions are caused by the mobility of light groups in the molecule. The work of Barlow (*Proc. Roy. Dub. Soc.*, 1897, 8, 527) indicates clearly that the fact that simple substances, such as carbon tetrabromide, do not always crystallise in the cubic system, which was previously relied upon as a powerful argument in favour of Le Bel's view, is really without bearing on the question. The velocity with which inversion occurs in an optically active ammonium compound is more reasonably correlated with the velocity of dissociation into tertiary base and alkyl salt than with great mobility of the groups attached to the nitrogen atom.

Since information on this question might possibly accrue from experiments on the velocity of formation of the iodide in various solvents, 10 grams of benzylmethylaniline were dissolved with the equivalent quantity of allyl iodide in (*a*) 50 grams of ether, (*b*) 50 grams of absolute alcohol, and (*c*) 50 grams of carefully purified chloroform. After 48 hours at the ordinary laboratory temperature, solution *a* had deposited 1·8 grams of white, crystalline iodide, solution *b*, 12·6 grams of colourless iodide in crystals, some of which were 5 millimetres long, whilst solution *c* had naturally deposited no iodide, although practically complete interaction had occurred, as was shown when the chloroform solution was evaporated, the residue being crystalline, and only very slightly gummy. Formation of the iodide takes place most rapidly in chloroform, somewhat less so in alcohol, and far more slowly in dry ether; these experiments on the relative velocities of combination afford no information as to the velocity of dissociation, but merely support Menschutkin's demonstration of the great influence

exerted by solvents on the velocity of formation of quaternary ammonium compounds (*Zeit. physikal. Chem.*, 1890, **6**, 41 ; 1895, **16**, 193). That Menschutkin's quantitative experiments do not indicate a reversal of the combination scarcely affects the question, because similar determinations of the velocity of combination of ammonia with sulphuric acid would indicate no reversal unless made with an accuracy as yet impossible ; but that such a reversal occurs is certain from the gradual loss of ammonia observed on boiling the solution.

It should be noted that Wedekind's iodide is most conveniently prepared in a state of purity by mixing the components in alcoholic solution, and leaving the mixture for several weeks ; the salt then separates in large, colourless crystals, and is not contaminated with the dark oil produced when Wedekind's original method of preparation is used.

l-*Benzylphenylallylmethylammonium Iodide.*

This substance was prepared from the corresponding *l*-camphorsulphonate in the same way as its enantiomorphously related isomeride. After several crystallisations from absolute alcohol, it melts at 147° with decomposition, and two successive crystallisations, *a* and *b*, gave the following rotatory power determinations :

a. 0·2604 gram, made up to 25·1 c.c. with cold chloroform at 17°, gave α_D −1·11° in a 2 dcm. tube ; whence $[\alpha]_D$ −53·4°.

b. 0·2511 gram, made up to 25·1 c.c. with cold chloroform at 17°, gave α_D −1·07° in a 2 dcm. tube ; whence $[\alpha]_D$ −53·4°.

Since the specific rotatory power is not altered by recrystallisation, the value given above would seem to apply to the pure compound ; it is noteworthy, however, that just as the purest sample of *l*-benzylphenylallylmethylammonium *l*-camphorsulphonate has a lower specific rotatory power than its enantiomorphously related isomeride, so the *l*-iodide gives a lower value than the *d*-iodide. This, too, in spite of the fact that the active iodides are far less soluble than the externally compensated substance.

l-Benzylphenylallylmethylammonium iodide undergoes and resists inversion under exactly the same conditions as its *d*-isomeride.

d-*Benzylphenylallylmethylammonium Bromide.*

d-Benzylphenylallylmethylammonium bromide was prepared from carefully purified *d*-camphorsulphonate as described by Pope and Peachey (*loc. cit.*, 1130), and by repeated crystallisations of the substance from absolute alcohol the melting point was raised to 165—167°. The quantity of material available was insufficient to allow of successive crystallisations being examined, but the following determination

of optical activity was made with salt which had been several times recrystallised from alcohol:

0·1237 gram, made up to 25·0 c.c. with cold chloroform at 16·5°, gave α_D +0·635° in a 2 dcm. tube; whence $[\alpha]_D$ +64·1°.

l-Benzylphenylallylmethylammonium Bromide.

This salt, after recrystallisation from absolute alcohol, melts at 166—168° and a solution of 0·1466 gram, made up to 25·1 c.c. with cold chloroform at 17°, gave α_D −0·76° in a 2 dcm. tube; whence $[\alpha]_D$ −65·0°. The result of this determination is numerically identical within the limits of experimental error with that obtained for the enantiomorphously related salt.

On keeping the cold chloroform solutions of the *d*- and *l*-bromides, inversion occurs in just the same way as with the iodides; the inversion, however, takes place rather more slowly in the case of the bromides, requiring six days for its completion at the ordinary laboratory temperature in the dark.

Crystalline Form of the d-, l-, *and* i-*α-Benzylphenylallylmethylammonium Bromides.*

The optically active bromides crystallise from aqueous solution in lustrous prisms very closely resembling the crystals of the externally compensated substance measured by Fock (*Ber.*, 1899, **32**, 3561). As predominant forms they exhibit $m\{110\}$, $n\{120\}$, and $r\{101\}$, whilst the pinacoids $a\{100\}$ and $b\{010\}$ are small and not always present. The forms $s\{201\}$ and $o\{121\}$ are very rarely observed, and the faces of $o\{121\}$, when present, are observed as the two enantiomorphously related sphenoids $o+\kappa\{121\}$ and $o-\kappa\{121\}$, the former being exhibited by crystals of the *d*-bromide (Fig. 1) and

Fig. 1.

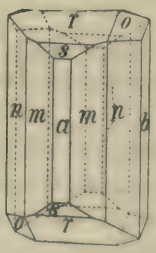
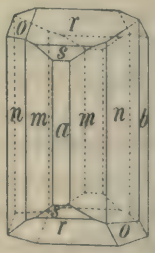


Fig. 2.



the latter by those of the *l*-bromide (Fig. 2) only. It is thus proved that the two substances crystallise in enantiomorphously related forms, and it is hence concluded that Pasteur's law applies, not only to

optically active substances containing an asymmetric carbon atom, but also to substances which owe optical activity to the presence of an asymmetric nitrogen atom.

Crystalline system.—Orthorhombic: Sphenoidal Hemihedrism.

$$a : b : c = 0{\cdot}8844 : 1 : 0{\cdot}6562.$$

Forms observed on *d*-bromide.—*a*{100}, *b*{010}, *m*{110}, *n*{120}, *r*{101}, *s*{201}, $o + \kappa$\{121\}.

Forms observed on *l*-bromide.—*a*{100}, *b*{010}, *m*{110}, *n*{120}, *r*{101}, *s*{201}, $o - \kappa$\{121\}.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
rr =101 : $\bar{1}01$	26	72°49′— 73°24′	73° 9′	—
rs =101 : 201	9	19 6 — 19 39	19 24	19°27′
ar =100 : 101	7	53 16 — 53 42	53 29	53 25
as =100 : 201	5	33 31 — 34 2	33 47	35 58
bn =010 : 120	29	29 18 — 29 46	29 29	—
mn =110 : 120	14	18 49 — 19 30	19 11	19 2
mm =110 : $1\bar{1}0$	11	82 41 — 83 15	83 4	82 59
am =100 : 110	6	41 0 — 41 56	41 24	41 29
mr =110 : 101	8	63 4 — 63 39	63 20	63 29
ms =110 : 201	4	51 27 — 52 2	51 44	51 36
bo =010 : 121	19	43 8 — 43 57	43 30	43 30
ro =101 : 121	14	46 4 — 46 42	46 28	46 30
mo =110 : $\bar{1}21$	7	37 34 — 38 25	37 55	38 2
oo =121 : $\bar{1}\bar{2}1$	9	112 30 —113 26	112 59	112 53
no =120 : 121	8	32 49 — 33 57	33·24	33 33

The measurements given above for the active bromides are, within the limits of experimental error, identical with those obtained by Fock (*loc. cit.*) from crystals of the externally compensated salt. This is evident from the following table, which gives the corresponding numerical values obtained by Fock and by us. A slight difference is observed in that Fock's crystals showed a smaller number of

	d- and *l*-. P. and H.	Inactive. Fock.
a : b : c	0·8844 : 1 : 0·6562	0·8889 : 1 : 0·6585
mm =110 : $1\bar{1}0$	82°59′	83°16′
rr =101 : $\bar{1}01$	73 9	73 4
bn =010 : 120	29 29	29 23
rm =101 : 110	63 29	63 33

forms than do those of the active substances; this is perhaps due to the greater solubility of the externally compensated substance. The optical properties as given by Fock are also confirmed by observations made on our own crystals. It follows that the inactive salt is not a racemic compound but is either pseudoracemic (Kipping and Pope, Trans., 1897, 71, 989) or a mere mechanical mixture of the two component salts. This, as has been previously pointed out, is also true for the corresponding iodides (Pope and Peachey, Trans., 1899, 75, 1129).

Inactive Benzylphenylallylmethylammonium Nitrate,
$C_6H_5 \cdot CH_2 \cdot N(C_6H_5)(C_3H_5)(CH_3) \cdot NO_3$.

On treating the hot alcoholic solution of the externally compensated iodide with one molecular proportion of silver nitrate dissolved in the minimum quantity of water, filtering from silver iodide, and evaporating to dryness, a crystalline residue is obtained which may be purified by crystallisation from boiling moist acetone. It forms colourless, microscopic needles melting at 153—154° with decomposition and is very soluble in alcohol or water.

0·1634 gave 0·4059 CO_2 and 0·1037 H_2O. C = 67·75; H = 7·05.
$C_{17}H_{20}O_3N_2$ requires C = 67·94; H = 6·69 per cent.

d-*Benzylphenylallylmethylammonium nitrate,*
$C_6H_5 \cdot CH_2 \cdot N(C_6H_5)(C_3H_5)(CH_3) \cdot NO_3$.

It seemed desirable to prepare from the active haloid salts a salt soluble in water which should contain no asymmetric carbon atom, in order that a direct determination of the rotatory power of the basic ion might be made for the confirmation or otherwise of the value deduced from the examination of the *d*-camphorsulphonate. The nitrate was therefore prepared by boiling equivalent proportions of *d*-benzylphenylallylmethylammonium iodide and finely powdered silver nitrate in a mixture of alcohol and acetone until reaction was complete. After filtration and evaporation to dryness, the crystalline residue was dissolved in a little dry acetone and dry ether added to the warm solution; on strongly cooling, *d*-benzylphenylallylmethylammonium nitrate separated in colourless, microscopic needles and was further purified by several repetitions of the same process. The salt seems much more soluble than the externally compensated isomeride, and melts at 164—165°.

0·1592 gave 0·3958 CO_2 and 0·1000 H_2O. C = 67·81; H = 6·98.
$C_{17}H_{20}O_3N_2$ requires C = 67·94; H = 6·69 per cent.

The following rotatory power determinations were made with two

successive crystallisations, *a* and *b*, of material which had already been several times recrystallised.

(*a*). 0·1956 gram, made up to 25·1 c.c. with cold water at 11·5°, gave α_D +0·86° in a 2 dcm. tube; whence $[\alpha]_D$ +55·2° and $[M]_D$ +165·4°.

(*b*). 0·3217 gram, made up to 25·1 c.c. with cold water at 14°, gave α_D + 1·41° in a 2 dcm. tube; whence $[\alpha]_D$ +55·0° and $[M]_D$ +165·0°.

The mean value for the molecular rotatory power of the basic ion is thus $[M]_D$ +165·2°, a value which compares well with that deduced from the examination of the *d*-camphorsulphonate, namely, $[M]_D$ +166·5°.

The fact that asymmetrically substituted ammonium salts exhibit optical activity, more especially when taken in conjunction with the tetrahedral configuration of sulphonium compounds (Pope and Peachey, Trans., 1900, 77, 1072), proves conclusively the incorrectness of Kekulé's view that ammonium salts are mere molecular compounds in which the two constituent parts preserve their individual molecular existence; such ammonium salts owe their occurrence to the operation of the ordinary valency laws, and nitrogen is either ter- or quinquevalent according to its state of combination. This being clearly true, it becomes interesting to inquire whether, in substances like the substituted ammonium platinichlorides or mercuriodides, the nitrogen assumes a higher valency than five; this question must be considered partly in the light of the simpler stereo-relations holding amongst sulphur compounds. It is customary to suppose that in simple molecules containing bivalent sulphur, such as that of hydrogen sulphide, the three component atoms lie along a straight line, and this view derives support from the absence of evidence that any isomerism of a *syn-* and *anti-* nature occurs amongst organic sulphides or related substances. But since the asymmetric quadrivalent sulphur atom gives rise to enantiomorphism, it is hardly possible that any two of the valency directions of quadrivalent sulphur lie in a straight line; during the transition from bi- to quadri-valence, a change in, or redistribution of, the valency directions has thus apparently taken place. A new principle may therefore be stated as probably true—that when an element changes in valency the original valency directions may also change; the necessity for this is not obviated by aid of the speculations of Wunderlich concerning the composite nature of sulphur and nitrogen atoms (*Configuration organischer Molekule, Würzburg*, 1886), because the validity of these is already disproved by the discovery of enantiomorphism amongst sulphonium and ammonium derivatives. The introduction of this new factor invalidates the conclusions drawn by Hantzsch, Behrend, and others, from their inability

to resolve tertiary bases into optically active components by crystallising their salts with active acids, that the three nitrogen valencies in amines lie in a plane, and also explains the well-known fact that a bivalent sulphur atom in a closed ring cannot combine with an alkyl iodide and become quadrivalent.* Further, it would seem that if the valency of sulphur or of nitrogen changes during formation of a platinichloride or mercuriodide from an optically active sulphonium or ammonium salt, inversion would very probably accompany the change. Suppose, for instance, that the tetrahedrally environed quadrivalent sulphur atom in an optically active sulphonium compound becomes sexavalent by addition of mercuric iodide, and that, in the mercuriodide, the six groups attached to the sulphur atom are situated at the apices of an octahedron, the four groups originally contained in the sulphonium compound then necessarily lie in a plane with the sulphur atom, and if they attain that position before the elements of mercuric iodide become finally attached, the enantiomorphism disappears. Not only should this result from the deflection of the valency directions which, by their original positions, determined the optical activity, but inversion would probably be expected to accompany the intramolecular turmoil attending the change of valency. When, therefore, it is proved, as is done below, that no trace of inversion attends the formation of *d*-benzylphenylallylmethylammonium mercuriodide, the view that such substance contains septavalent nitrogen is rendered highly improbable.

The following compounds were made for the purpose of testing these points.

d-*Benzylphenylallylmethylammonium Platinichloride*,
$2C_6H_5\cdot CH_2\cdot N(C_6H_5)(C_3H_5)(CH_3)Cl,PtCl_4$.

This salt separates as a light yellow, microcrystalline powder on adding hydrochloric acid and platinic chloride successively to an aqueous solution of *d*-benzylphenylallylmethylammonium *d*-camphorsulphonate; it is insoluble in all the ordinary solvents, and its rotatory power could consequently not be ascertained.† After well washing with water and drying, it blackens at 155° and melts at 165°; according to Wedekind (*loc. cit.*, 51), the corresponding inactive salt melts at 162—163°. The active salt was found to contain 22·4 per cent. of Pt, instead of the calculated 22·1 per cent.

* We have ourselves been quite unable to induce any interaction between β-methylthiophen and bromoacetic acid, phenacyl bromide, methyl iodide, or allyl iodide.

† We have observed that many substances, such as platinichlorides, which are ordinarily sparingly soluble, dissolve freely in epichlorhydrin; this particular salt, however, is not soluble in this medium.

d-*Benzylphenylallylmethylammonium Mercuriodide*,
$C_6H_5 \cdot CH_2 \cdot N(C_6H_5)(C_3H_5)(CH_3)I,HgI_2$.

On heating a mixture of *d*-benzylphenylallylmethylammonium iodide and mercuric iodide, in molecular proportion, with ethyl acetate, it quickly dissolves and, on cooling, the mercuriodide is deposited as sulphur-yellow, crystalline scales. After several recrystallisations from hot ethyl acetate, it melts constantly at 125—126°, whilst the corresponding inactive salt, similarly prepared and possessing very similar properties, melts at 118—120°. The active salt is sparingly soluble in most organic solvents, and is converted into a pasty, yellow mass by water. The following rotatory power determinations were made with two successive crystallisations, *a* and *b*, from ethyl acetate, of a sample which had already been several times recrystallised :

(*a*). 0·1956 gram, made up to 25·0 c.c. with ethyl acetate at 14°, gave α_D +0·38° in a 2 dcm. tube; whence $[\alpha]_D$ +24·3°.

(*b*). 0·2028 gram, made up to 25·0 c.c. with ethyl acetate at 18·5°, gave α_D +0·40° in a 2 dcm. tube; whence $[\alpha]_D$ +24·6°.

The substance thus has the mean specific rotatory power $[\alpha]_D$ +24·4° in ethyl acetate solution, and on calculating the value on the *d*-benzylphenylallylmethylammonium iodide which it contains, the value $[\alpha]_D$ +54·7° is obtained; the latter number corresponds very closely with the specific rotatory power of the iodide in chloroform solution. The iodide is too sparingly soluble in ethyl acetate to allow of rotatory power determinations being made, and the same is true of the mercuriodide in chloroform. The mercuriodide is difficult to analyse, but the following rotatory power determination proves its composition, and at the same time shows that no trace of inversion attends the conversion of the *d*-iodide into the *d*-mercuriodide.

0·0912 gram of *d*-iodide of $[\alpha]_D$ +55·2°, and 0·1135 gram of mercuric iodide, made up to 25·0 c.c. with ethyl acetate at 15°, gave α_D +0·40° in a 2 dcm. tube; whence the value $[\alpha]_D$ +54·8° for the *d*-iodide and the value $[\alpha]_D$ +24·4° for the mercuriodide, supposing the latter to consist of the above equivalent weights of *d*-iodide and mercuric iodide. If, in the preparation of the mercuriodide, less than a molecular proportion of the *d*-iodide is used, a yellow mass remains insoluble in the ethyl acetate, whilst if a slight excess of mercuric iodide is used, this salt remains undissolved.

l-*Benzylphenylallylmethylammonium Mercuriodide*,
$C_6H_5 \cdot CH_2 \cdot N(C_6H_5)(C_3H_5)(CH_3)I,HgI_2$.

This salt, prepared in the same way as the preceding one, also crystallises in yellow scales melting at 125—126°; the following deter-

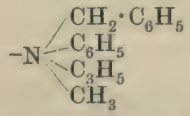
minations were made with two successive crystallisations, *a* and *b*, of a carefully purified sample :

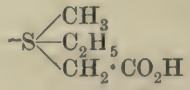
(*a*). 0·2017 gram, made up to 25·0 c.c. with ethyl acetate at 14·5°, gave α_D −0·38° in a 2 dcm. tube ; whence $[\alpha]_D$ −23·5°.

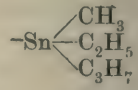
(*b*). 0·2020 gram, made up to 25·0 c.c. with ethyl acetate at 14·5°, gave α_D −0·37° in a 2 dcm. tube ; whence $[\alpha]_D$ −22·9°.

The result is thus obtained that, during the formation of a mercuriiodide from *d*- or *l*-benzylphenylallylmethylammonium iodide, the optical activity persists, and this fact, if the principle previously laid down concerning the change of valency direction accompanying change of valency be accepted, lends a high measure of probability to the view that, in compounds of the type of an ammonium mercuriodide, the nitrogen is still quinquevalent. This conclusion is of importance, because the sulphonium iodides yield mercuriodides so similar to the ammonium mercuriodides that any argument concerning the one should be directly applicable to the other class of compounds ; Smiles has argued (Trans., 1900, **77**, 160) that the sulphonium mercuriodides contain sexavalent sulphur, following in this Dobbin and Masson (Trans., 1885, **47**, 56), who suggested the possible hexadic nature of the sulphur in sulphonium trihalogen compounds, and, as a sequence, that the ammonium dichloroiodide discovered by Tilden (Trans., 1866, **19**, 145) may contain septavalent nitrogen. The facts now brought forward must be considered as rendering highly improbable the supposition that, in the compounds mentioned, sulphur and nitrogen exist as hexadic and heptadic elements respectively.

The optically active quaternary ammonium derivatives share with the optically active tin and sulphur compounds a constitutional peculiarity of considerable interest ; they are all salt-like substances in which the acidic part of the molecule is immediately connected with the asymmetric atom. They are thus electrolytes, and if it be supposed that they undergo electrolytic dissociation in aqueous solution, the ionic scission must take place between the acidic group and the asymmetric atom ; the basic ion will thus consist of a nitrogen atom attached to four atomic groups, but having one bond free. Applying this to the asymmetric sulphur and tin compounds also, the following ions exhibit optical activity :







In these ions, tin and sulphur atoms attached to only *three*, and a nitrogen atom attached to only *four*, atomic groups exhibit optical

activity. The abnormal condition of an asymmetric atom of which one bond is free seems to be accompanied by no particularly marked tendency towards optical inversion. In these facts should be found the basis of an experimental method of directly verifying the truth of our current views concerning the nature of ions; these views, being derived from the consideration of facts somewhat remotely connected with the prime cause, are at present without an absolutely fundamental experimental basis.

Our thanks are due to the Research Fund Committee of the Chemical Society for grants defraying the cost of materials used in this investigation.

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LXXXIX.—*Hydroxyoxamides.*

By ROBERT HOWSON PICKARD, D.Sc., Ph.D., and WILLIAM CARTER.

ROTERMUND (*Annalen*, 1875, **175**, 313) showed that an aqueous solution of the potassium salt of dibenzhydroxamic acid evolves carbon dioxide and yields *s*-diphenylcarbamide and potassium benzoate. Thiele and one of us subsequently (*Annalen*, 1899, **309**, 189) have shown that, in general, the salts of acylhydroxamic acids easily decompose, forming carbimides, which, in presence of water, yield carbon dioxide and a *s*-disubstituted carbamide; in presence of an alcohol, the corresponding carbamate; and in presence of ammonia, a monosubstituted carbamide, thus, for example:

$$C_6H_5\cdot C(OK):NOAc \longrightarrow KOAc + (C_6H_5\cdot CNO) \longrightarrow C_6H_5\cdot NCO;$$
$$C_6H_5\cdot NCO + HOEt = C_6H_5\cdot NH\cdot CO_2Et.$$

Since it is not necessary to isolate the carbimides formed in the course of these reactions in order to obtain the carbamides, &c., this method appeared a suitable one for preparing from monohydroxyoxamides the monosubstituted biurets and allophanates, of which up to the present only the phenyl derivatives are known.

Monohydroxyoxamides, $R\cdot NH\cdot CO\cdot CO\cdot NH\cdot OH$, are quantitatively obtained by the hydrolysis of ethyl oxamates, $R\cdot NH\cdot CO\cdot CO_2Et$, with an anhydrous alcoholic solution of hydroxylamine; they have all the characteristics of hydroxamic acids, giving cherry-red colorations with ferric chloride, and forming insoluble, grass-green, copper salts;

they easily form acetyl derivatives, $RNH\cdot CO\cdot C(OH){:}NOAc$, which are well defined, crystalline substances, do not give the characteristic reactions of hydroxamic acids, are, however, acid in reaction, and form well-defined, crystalline salts.

The salts of acetylhydroxyoxamides decompose in presence of water, yielding compounds of the type of carbonyldicarbamide,

$$CO(NH\cdot CO\cdot NH_2)_2;$$

when boiled with water containing a little ammonia, they decompose, often with great violence, giving quantitative yields of monosubstituted biurets, $R\cdot NH\cdot CO\cdot NH\cdot CO\cdot NH_2$. Similarly, when these salts are boiled with ethyl alcohol, the corresponding allophanate,

$$R\cdot NH\cdot CO\cdot NH\cdot CO_2Et,$$

is obtained.

Hydroxyoxamide.

Hydroxyoxamide, $NH_2\cdot CO\cdot CO\cdot NH\cdot OH$, has been prepared by Schiff and Monsacchi (*Annalen*, 1895, **288**, 290). The yield is quantitative, if the oxamethane is hydrolysed with an anhydrous alcoholic * solution of hydroxylamine. The acetyl derivative (*loc. cit.*) gives an acid reaction with litmus, but is so very slightly soluble in water or alcohol that the preparation of any salts was impossible. When the acetyl derivative is warmed with the calculated quantity of sodium carbonate solution, it dissolves, and a very violent reaction starts. When this is over, small crystals of carbonyldicarbamide (Schmidt, *J. pr. Chem.*, 1872, [ii], **5**, 39) are deposited. This was identified by its solubilities, and by the fact that, when warmed with potash, it yielded ammonia and cyanuric acid.

A quantitative yield of biuret is obtained when acetylhydroxyoxamide is boiled with a dilute solution of ammonia. The acetyl compound dissolves, a very vigorous reaction ensues, and on cooling the solution deposits long, acicular crystals of biuret. This was identified by its melting point, the reaction with copper sulphate and potassium hydroxide, and the following analysis:

0·1059 gave 31·6 c.c. moist nitrogen at 14° and 756 mm. N = 34·92.

$C_2H_5O_2N_3,H_2O$ requires N = 34·71 per cent.

Phenylhydroxyoxamide.

Phenylhydroxyoxamide (Schiff and Monsacchi, *loc. cit.*) is obtained quantitatively by the hydrolysis of ethyl oxanilate with an anhydrous alcoholic solution of hydroxylamine. The acetyl derivative is acid in properties and slightly soluble in alcohol. When the calculated

* Commercial methylated spirit distilled first over lime and then over calcium arbide was used.

quantity of sodium dissolved in anhydrous alcohol is added to an anhydrous alcoholic solution of the acetyl compound, the *sodium* salt is precipitated as a colourless, gelatinous mass; this explodes when heated, and is soluble in water, giving an alkaline solution.

0·4705 gave 0·1423 Na_2SO_4. Na = 9·79.
$C_{10}H_9O_4N_2Na$ requires Na = 9·42 per cent.

Carbonyldiphenylcarbamide, $CO(NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5)_2$, is precipitated when an aqueous solution of the sodium salt of phenylacetylhydroxyoxamide is warmed on a water-bath for half an hour. It crystallises from alcohol in large, prismatic needles which melt at 140°.

0·2080 gave 0·4592 CO_2 and 0·0900 H_2O. C = 60·20; H = 4·80.
0·1612 gave 26·6 c.c. moist nitrogen at 17° and 754 mm. N = 18·99
$C_{15}H_{14}O_3N_4$ requires C = 60·40; H = 4·69; N = 18·79 per cent.

It is slightly soluble in hot water, and when boiled with hydrochloric acid yields carbon dioxide, ammonium chloride, and aniline hydrochloride. *Monophenylbiuret*, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, is precipitated when a solution of phenylacetylhydroxyoxamide in dilute ammonia is warmed. It crystallises from water in slender needles which melt and decompose at 150°; when crystallised from chloroform, it melts at 154° and decomposes at 156°.

0·1310 gave 0·2570 CO_2 and 0·0628 H_2O. C = 53·50; H = 5·32.
0·1256 ,, 25·6 c.c. moist nitrogen at 13° and 733 mm. N = 23·20.
$C_8H_9O_2N_3$ requires C = 53·63; H = 5·02; N = 23·46 per cent.

When heated with aniline, monophenylbiuret yields ammonia and *s*-diphenylbiuret (m. p. 210°), so that it appears to be identical with the product obtained by Weith (*Ber.*, 1877, 10, 1744) by the action of phosphorus trichloride on phenylcarbamide.

p-*Tolylhydroxyoxamide.*

p-*Tolylhydroxyoxamide*, $CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}OH$, is obtained in the form of an amorphous hydroxylamine salt, when ethyl *p*-tolyloxamate (1 mol.) dissolved in anhydrous alcohol is hydrolysed with an anhydrous alcoholic solution of hydroxylamine (2 mols.). The hydroxyoxamide is obtained by boiling the hydroxylamine salt with dilute acetic acid. It crystallises from acetic acid in clusters of beautiful, slender needles or in laminæ with a pearly lustre, and melts and decomposes at 155°.

0·1788 gave 22·8 c.c. moist nitrogen at 17° and 742 mm. N = 14·44.
$C_9H_{10}O_3N_2$ requires N = 14·43 per cent.

It gives the coloration with ferric chloride characteristic of

hydroxamic acids, and when boiled with its own weight of a mixture of equal parts of acetic anhydride and glacial acetic acid yields

p-*Tolylacetylhydroxyoxamide*, $CH_3 \cdot C_6H_4 \cdot CO \cdot C(OH) : NO \cdot CO \cdot CH_3$, which crystallises from acetic acid in shining laminæ melting and decomposing at 178°.

0·1483 gave 15·4 c.c. moist nitrogen at 17° and 752 mm. N = 11·92.

$C_{11}H_{12}O_4N_2$ requires N = 11·86 per cent.

It is moderately soluble in hot alcohol, and when neutralised with alcoholic solutions of ammonia and sodium ethoxide forms well-defined salts. The *ammonium* salt crystallises in lustrous laminæ which decompose at 137·5°. The *sodium* salt is a microcrystalline powder; this dissolves easily in water, and the solution, when boiled, deposits

Carbonyldi-p-*tolylcarbamide*, $CO(NH \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_3)_2$, which crystallises from dilute alcohol in prismatic needles melting at 170°.

0·1300 gave 19·6 c.c. moist nitrogen at 17° and 746 mm. N = 17·16.

$C_{17}H_{18}O_3N_4$ requires N = 17·17 per cent.

The sodium salt of *p*-tolylacetylhydroxyoxamide dissolves in absolute ethyl alcohol after boiling for some hours, and the solution then contains sodium acetate and

Ethyl p-*tolylallophanate*, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot NH \cdot CO_2 \cdot C_2H_5$, which is obtained by extracting with ether the residue left after evaporation of the alcohol. It crystallises in long, white, acicular needles and melts at 145°.

0·1641 gave 18·3 c.c. moist nitrogen at 17° and 760 mm. N = 12·94.

$C_{11}H_{14}O_3N_2$ requires N = 12·61 per cent.

When heated at 100° for six hours in a sealed tube with concentrated aqueous ammonia, it is converted into

p-*Tolylbiuret*, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot NH \cdot CO \cdot NH_2$, which is, however, best prepared by boiling a solution of the ammonium salt of *p*-tolylacetylhydroxyoxamide in dilute aqueous ammonia. It crystallises in needles from dilute ammonia or alcohol and melts and decomposes at 194°.

0·1241 gave 23 c.c. moist nitrogen at 17° and 760 mm. N = 21·50.

$C_9H_{11}O_2N_3$ requires N = 21·76 per cent.

It is insoluble in ether, and does not give the biuret reaction.

α-Naphthylhydroxyoxamide.

α-Naphthylhydroxyoxamide, $C_{10}H_7 \cdot NH \cdot CO \cdot CO \cdot NH \cdot OH$, is obtained in an analogous manner to the *p*-tolyl compound by the hydrolysis of

ethyl α-naphthyloxamate with hydroxylamine. The *hydroxylamine* salt melts and decomposes at 152°, and when boiled with dilute acetic acid is converted into the hydroxyoxamide. This crystallises from acetic acid in needles which melt at 172°.

0·1071 gave 11·4 c.c. moist nitrogen at 16° and 745·5 mm. N = 12·16.
$C_{12}H_{10}O_3N_2$ requires N = 12·17 per cent.

It gives the coloration with ferric chloride characteristic of hydroxamic acids, is slightly soluble in most organic solvents, and when boiled with acetic anhydride and glacial acetic acid yields

α-Naphthylacetylhydroxyoxamide, $C_{10}H_7{\cdot}NH{\cdot}CO{\cdot}C(OH){:}NO{\cdot}CO{\cdot}CH_3$, which crystallises in clusters of felted and silky needles and melts and decomposes at 170°.

0·1478 gave 12·9 c.c. moist nitrogen at 16° and 746 mm. N = 9·98.
$C_{14}H_{12}O_4N_2$ requires N = 10·25 per cent.

The *sodium* salt is deposited in lustrous laminæ, when an alcoholic solution is neutralised with sodium ethoxide. The *ammonium* salt crystallises from anhydrous alcohol in needles which melt and decompose at 140—141°.

Carbonyldi-α-naphthylcarbamide, $CO(NH{\cdot}CO{\cdot}NH{\cdot}C_{10}H_7)_2$, is precipitated when an aqueous solution of the sodium salt of α-naphthylacetylhydroxyoxamide is boiled. It crystallises from dilute alcohol in rosettes of lustrous needles, melts at 202—203°, then solidifies, and is still solid at 290°.

0·1795 gave 22·4 c.c. moist nitrogen at 16° and 746 mm. N = 14·27.
$C_{23}H_{18}O_3N_4$ requires N = 14·07 per cent.

Ethyl α-naphthylallophanate, $C_{10}H_7{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO_2{\cdot}C_2H_5$, is obtained in an analogous manner to the tolylallophanate. It crystallises from ether, light petroleum, or benzene in long, prismatic needles and melts at 170—170·5°.

0·1407 gave 13·2 c.c. moist nitrogen at 18° and 752 mm. N = 10·72.
$C_{14}H_{14}O_3N_2$ requires N = 10·85 per cent.

When heated in a sealed tube at 100° for 6 hours with concentrated aqueous ammonia, it is converted into

α-Naphthylbiuret, $C_{10}H_7{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, which is also readily obtained by boiling an aqueous solution of the ammonium salt of α-naphthylacetylhydroxyoxamide with a solution of ammonium carbonate. It crystallises from alcohol in small needles which melt at 210—211°.

0·1119 gave 17·7 c.c. moist nitrogen at 16° and 746 mm. N = 18·09.
$C_{12}H_{11}O_2N_3$ requires N = 18·34 per cent.

It is slightly soluble in water and ether, but does not give the biuret reaction.

β-Naphthylhydroxyoxamide.

β-Naphthylhydroxyoxamide, $C_{10}H_7 \cdot NH \cdot CO \cdot CO \cdot NH \cdot OH$, is easily obtained by the hydrolysis of ethyl β-naphthyloxamate* with hydroxylamine. It crystallises from dilute acetic acid, and melts and decomposes at 174°.

0·1858 gave 20 c.c. moist nitrogen at 17° and 740 mm. N = 12·15.
$C_{12}H_{10}O_3N_2$ requires N = 12·17 per cent.

The *acetyl* derivative crystallises from acetic acid in needles, and melts and decomposes at 172°.

0·2079 gave 18·6 c.c. moist nitrogen at 15° and 740 mm. N = 10·19.
$C_{14}H_{12}O_4N_2$ requires N = 10·25 per cent.

The *ammonium* salt crystallises in lustrous laminæ, and melts and decomposes at 140°. The *sodium* salt was obtained as a microcrystalline powder.

The following compounds were obtained by methods analogous to those used for preparing the α-naphthyl compounds.

Carbonyldi-β-naphthylcarbamide, $CO(NH \cdot CO \cdot NH \cdot C_{10}H_7)_2$, crystallises from dilute alcohol in needles which soften at 213° and decompose at about 290°.

0·1014 gave 12·4 c.c. moist nitrogen at 19·5° and 760 mm. N = 14·02.
$C_{23}H_{18}O_3N_4$ requires N = 14·07 per cent.

Ethyl β-naphthylallophanate, $C_{10}H_7 \cdot NH \cdot CO \cdot NH \cdot CO_2C_2H_5$, crystallises from alcohol in prismatic needles and melts at 140°.

0·1579 gave 15·3 c.c. moist nitrogen at 19° and 756 mm. N = 11·08.
$C_{14}H_{14}O_3N_2$ requires N = 10·85 per cent.

β-Naphthylbiuret, $C_{10}H_7 \cdot NH \cdot CO \cdot NH \cdot CO \cdot NH_2$, crystallises from alcohol in small prisms which melt and decompose at 203°.

0·1301 gave 20·4 c.c. moist nitrogen at 14° and 742 mm. N = 18·09.
$C_{12}H_{11}O_2N_3$ requires N = 18·34 per cent.

s-Dihydroxyoxamide, $OH \cdot NH \cdot CO \cdot CO \cdot NH \cdot OH$ (oxaldihydroxamic acid), has been prepared by Hantzsch (*Ber.*, 1894, **27**, 801), who has

* No descriptions of *ethyl β-naphthyloxamate* and *s-di-β-naphthyloxamide* are to be found in the literature. These substances are easily prepared by heating calculated quantities of β-naphthylamine and ethyl oxalate and are easily separated, since the oxamide is practically insoluble in alcohol. The oxamide crystallises from toluene in silky needles and melts at 274—275°. The oxamate crystallises in needles from alcohol and melts at 121°.

also described a tetracetate (m. p. 141°). This acetate, however, appears to be a diacetate of the formula $[C(OH):NOAc]_2$, since determinations of its molecular weight in acetic acid solution, by the freezing point method, gave 202 and 210 (the diacetate would have a molecular weight 204 and the tetracetate 312). Further, this diacetate has a slightly acid reaction and dissolves in a solution of sodium carbonate; the resulting solution, after warming, contains small quantities of *hydrazine*; the presence of hydrazine in the solution was proved by the reduction of Fehling's solution and the formation of benzalazine (m. p. 92°) when the solution was shaken with benzaldehyde. The formation of hydrazine can be explained by the general reaction of hydroxamic acids, thus:

$$[C(ONa):NOAc]_2 \rightarrow (ONC\cdot CNO) \rightarrow OCN\cdot NCO.$$
$$OCN\cdot NCO + 2H_2O = N_2H_4 + 2CO_2.$$

The preliminary work in connection with this research was carried out by one of us (R. H. P.) when holder of a Priestley Research Scholarship at Mason University College.

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XC.—*Note on Pyromucylhydroxamic Acid.*

By Robert Howson Pickard, D.Sc., Ph.D., and Allen Neville, B.Sc.

The reactions of pyromucylhydroxamic acid have been studied with the view of obtaining the furfuran-carbamides and -carbamates by Thiele and Pickard's method (*Annalen*, 1899, **309**, 189). These are, however, uncrystallisable oils, which decompose on hydrolysis (compare Freundler, *Bull. Soc. Chim.*, 1897, [iii], **17**, 419).

Pyromucylhydroxamic acid, $C_4H_3O\cdot CO\cdot NH\cdot OH$, is formed when ethyl pyromucate * is hydrolysed with an anhydrous alcoholic solution of hydroxylamine. By precipitation with a solution of copper acetate, the grass-green copper salt is obtained, which is then suspended in alcohol and decomposed by hydrogen sulphide; on evaporation, the filtered solution yields the hydroxamic acid, which crystallises from water in lustrous, white needles and melts at 124°.

* In preparing pyromucic acid by Frankland and Aston's method (Trans., 1901, **79**, 511), a better yield is obtained if the solution of the pyromucates and lime is just rendered acid (to litmus) and then concentrated before the pyromucic acid is liberated by the addition of more sulphuric acid.

0·1351 gave 0·2329 CO_2 and 0·0467 H_2O. C = 47·01; H = 3·84.
0·1686 „ 16·8 c.c. moist nitrogen at 14° and 727 mm. N = 11·20.
$C_5H_5O_3N$ requires C = 47·24; H = 3·93; N = 11·02 per cent.

It gives the usual cherry-red coloration with ferric chloride, is comparatively stable towards boiling hydrochloric acid, and at first the compound appeared to have an analogous constitution to the 5-phenyl-3-isoxazolone obtained by Ruhemann and Stapleton (Trans., 1900, 77, 239) by the action of hydroxylamine on ethyl phenylpropiolate. It was, however, proved to be a hydroxamic acid by comparing the properties of its benzoyl derivative with those of *5-phenyl-3-benzoyl-isoxazolone*.

Benzoylpyromucylhydroxamic acid, $C_4H_3O{\cdot}C(OH){:}NO{\cdot}CO{\cdot}C_6H_5$, is precipitated when an aqueous solution of the hydroxamic acid is shaken with the calculated quantity of benzoyl chloride and sodium acetate. It crystallises from alcohol in needles and melts at 134°.

0·2025 gave 10·9 c.c. moist nitrogen at 15° and 763 mm. N = 6·32.
$C_{12}H_9O_4N$ requires N = 6·06 per cent.

It has an acid reaction and dissolves in a solution of sodium carbonate, whilst the *monobenzoyl* derivative of *5-phenyl-3-isoxazolone*, which melts at 106°, is insoluble in the reagent.

The *sodium* and *ammonium* salts are precipitated when ether is added to their alcoholic solutions. An aqueous solution of the sodium salt, when boiled with water, evolves carbon dioxide, and an oil (containing nitrogen) is obtained when the solution is evaporated.

This oil is presumably the difurfurancarbamide, but decomposes completely when hydrolysed. No better success was attained on attempting to prepare the carbamates by boiling the sodium salt with alcohols.

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XCI.—*The Absorption Spectra of Cyanogen Compounds.*

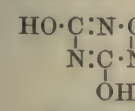
By WALTER NOEL HARTLEY, F.R.S.; JAMES J. DOBBIE, D.Sc., M.A., and ALEXANDER LAUDER, B.Sc.

THE following investigation was undertaken with the view of ascertaining whether, by an examination of the absorption spectra of the cyanogen compounds, it might be possible to throw some light upon the vexed question of the constitution of these substances.

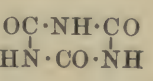
Some of the substances of a simple constitution belonging to this group had previously been examined. W. A. Miller and also L. Soret proved the transparency of hydrocyanic acid and the cyanides (*Phil. Trans.*, 1862, 861 ; this Journ., 1864, **2**, 59 ; *Arch. Sci. Phys. Nat.* 1878, 61), and Hartley independently found that hydrocyanic acid is a remarkably diactinic substance which exhibits no trace of selective absorption (Trans., 1882, **41**, 45). Cyanuric acid, owing to difficulties in its examination arising out of its sparing solubility and the necessity for examining warm solutions, at first appeared to give evidence of selective absorption. It was subsequently proved, however, that there was no absorption band even in layers of liquid 200 mm. thick, but that the rays between wave-lengths 3330 and 2572, to where the spectrum was sharply cut off, were only feebly transmitted (Proc., 1899, **15**, 46). In the present research, some derivatives of cyanic acid have been included, but we have directed our attention chiefly to cyanuric acid, melamine, and their respective alkyl derivatives.

The derivatives of cyanic acid which were examined are highly diactinic, and show only general absorption.

Cyanuric acid is commonly represented as a closed chain compound in which the chain is formed of alternate atoms of carbon and nitrogen, united by alternate double and single bonds (formula I), and a similar structure is assigned to the methyl ester (methyl cyanurate, m. p. 135°), which is obtained from cyanuric chloride by the action of sodium methoxide. The methyl derivative (methyl *iso*cyanurate ; methyl tricarbimide ; m. p. 175°), on the other hand, which is prepared by the distillation of potassium cyanate with potassium methyl sulphate, is represented as a derivative of *iso*cyanuric acid (formula II), which contains three ketonic groups, and has the carbon and nitrogen atoms united by single bonds only. In this derivative, the alkyl groups are directly united to the nitrogen atoms.

I. 

Cyanuric acid.

II. 

iso-Cyanuric acid or tricarbimide.

Pyridine and dimethylpyrazine, in which there are carbon and nitrogen atoms, united by alternate double and single bonds,* exhibit strong and persistent absorption bands, the selective absorption being more marked in dimethylpyrazine (Trans., 1900, **77**, 846), which contains two nitrogen atoms, than in pyridine, which contains only one.

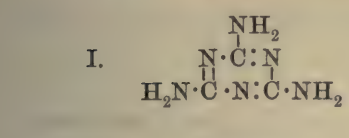
* That is, which possess the true benzenoid structure represented by alternate double and single bonds, or by the cyclic formula.

It was therefore to be expected that substances possessing the constitution assigned to normal cyanuric acid and its esters would likewise exhibit marked selective absorption, and that even to a greater degree than dimethylpyrazine.

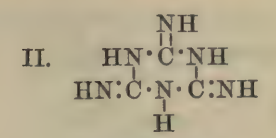
On the other hand, it was to be anticipated that the alkyl derivatives of *iso*cyanuric acid (formula II) would behave like piperidine and other substances composed of a closed chain of singly linked carbon and nitrogen atoms, or of a closed chain of singly linked carbon atoms, which exhibit general absorption only. All the cyanuric compounds, however, which we have examined show only general absorption, and give no indication of the presence of absorption bands. This result is what we anticipated in the case of derivatives of *iso*cyanuric acid, but so far as cyanuric acid and its esters are concerned, it is remarkable, especially when considered in connection with the fact that no strict experimental evidence has yet been advanced in support of the commonly received structural formula for cyanuric acid and its derivatives. The more complete study, therefore, of this acid and its derivatives renders doubtful the correctness of the formula which was deduced in the first instance from the examination of its optical properties.

Methyl cyanurate (m. p. 135°) yields cyanuric acid and methyl alcohol on hydrolysis with alkalis. It is therefore regarded as the ester of normal cyanuric acid (formula I), a conclusion which is supported by its method of formation from sodium methoxide and cyanuric chloride. Trimethylcarbimide (m. p. 175°), on the other hand, yields methylamine on treatment with alkalis, and is therefore regarded as a derivative of *iso*cyanuric acid (formula II). It is generally admitted, however, that chemical evidence of this kind is, in such cases, frequently misleading (Goldschmidt and Meissler, *Ber.*, 1890, **23**, 253; Michael, *J. pr. Chem.*, 1888, [ii], **37**, 513; Hartley and Dobbie, Trans., 1899, **75**, 640). In this instance, the spectrographic examination confirms the results arrived at on purely chemical grounds. The spectra of methyl cyanurate, m. p. 135°, bear a close resemblance to those of cyanuric acid, the absorption being somewhat greater owing to the replacement of three hydrogen atoms by three methyl groups. On the other hand, the spectra of trimethylcarbimide, m. p. 175°, notwithstanding a similar replacement of hydrogen by methyl groups, show considerably less absorption than those of cyanuric acid. In none of the cyanogen compounds is there any trace of an absorption band.

Melamine and its esters show only general absorption, the amount of absorption being somewhat greater than in the case of cyanuric acid. Melamine is regarded as the triamide of normal cyanuric acid (formula I).



Melamine
or cyanurtriamide.



*iso*Melamine
or *iso*cyanurtriimide.

The triethyl derivative (m. p. 74°), which is obtained by the action of ethylamine on cyanuric chloride, is, from its method of formation, considered to be a derivative of melamine; the ethyl derivative (m. p. 92°), on the other hand, which is prepared by the desulphurisation of thiourea, is regarded as a derivative of *iso*melamine. Here again the results of the spectrographic investigation are in accord with the conclusions arrived at on chemical grounds. The spectra of melamine and the triethyl derivative, m. p. 74°, are almost identical, whilst the general absorption exhibited by the spectra of the isomeric compound is considerably less.

The general result of the examination of these substances is in complete agreement with the views now generally held as to their relations to one another. As already observed, however, the absence of selective absorption is not in harmony with the constitution of cyanuric acid, as represented by a formula which is closely analogous to that of pyridine and still more closely to that of dimethylpyrazine. It may therefore be fairly considered as doubtful whether the constitution of cyanuric acid is rightly understood.

Experimental.

Potassium Cyanate.—Two specimens of potassium cyanate were examined; one obtained from Schuchardt of Görlitz, the other prepared by oxidising potassium ferrocyanide with manganese dioxide according to the method given by Wurtz (*Ann. Chem. Phys.*, 1854, [iii], 42, 44). This substance is highly diactinic, 50 mm. of a solution containing 1 milligram-molecule in 4 c.c. water, transmitting all rays to $^1/\lambda$ 4128 (λ 2422).

Potassium cyanate has also been examined by Soret (*Arch. Sci. Phys. Nat.*, 1893, [iii], 10, 429), who found that it gave a strong absorption band, of which we could find no indication.

In the preparation of ethylcarbimide from potassium cyanate and potassium ethyl sulphate, it is essential to the success of the experiment that the potassium cyanate should be freshly prepared. From this it might be supposed that the potassium cyanate undergoes some change on keeping. If this is the case, the change is not one which can be detected by means of the spectrograph, as we found the absorp-

tion spectra of specimens photographed immediately after preparation and again after standing for six months to be identical.

Ethyl iso*Cyanate; Ethylcarbimide, b. p.* 60°. *Methyl* iso*Cyanate; Methylcarbimide, b. p.* 44°.

These derivatives were prepared by the interaction of potassium cyanate with potassium ethyl sulphate and potassium methyl sulphate respectively (*Ann. Chem. Phys.*, 1854, [iii], 42, 43; *Chem. Centr.*, 1898, i, 445). As no suitable solvent could be found for these esters, they were photographed in thin layers.

Cyanuric Chloride.—This substance was prepared by passing dry chlorine and anhydrous hydrocyanic acid into dry chloroform, care being taken always to keep the chlorine in excess. The chloroform was evaporated in a current of dry air and the crystalline residue of cyanuric chloride purified by repeated crystallisation from carefully dried ether; it melted at 146°.

Cyanuric Acid.—Samples of cyanuric acid obtained from various sources as well as several specimens prepared by us from urea were examined and were found to give indentical spectra. Owing to the insolubility of cyanuric acid, considerable difficulty was experienced in making the spectroscopic examination. On this account, layers of greater thickness than usual of the cold saturated aqueous solution were employed, but no indication of selective absorption was observed. A layer 60 mm. in thickness of a solution containing 1 milligram-molecule in 60 c.c. of water transmits all rays to $^1/\lambda$ 3886 (λ 2573).

Methyl Cyanurate (m. p. 136°).—This substance was prepared by the interaction of sodium methoxide and cyanuric chloride. As will be seen from the curves, its spectra show close agreement with those of cyanuric acid. A layer 25 mm. in thickness of a solution containing 1 milligram-molecule in 20 c.c. of alcohol transmits all rays to $^1/\lambda$ 3922 (λ 2549).

Ethyl iso*Cyanurate; Ethyltricarbimide, m. p.* 95°. *Methyl* iso*Cyanurate; Methyltricarbimide, m. p.* 175°.

Two specimens of ethyl *iso*cyanurate were examined; one purchased from Schuchardt, the other obtained in the preparation of ethylcarbimide by the polymerisation of the latter substance. The photographs of the absorption spectra of the two specimens were identical. The specimen of methyl *iso*cyanurate examined was obtained in the same way during the preparation of methylcarbimide. The photographs of the trimethyl and triethyl derivatives show almost complete agreement. They are more highly diactinic than the corresponding derivatives of normal cyanuric acid.

Melamine.—The specimen examined was prepared by heating pure cyanuric chloride with excess of strong ammonia in a sealed tube at 100° for 5 hours. The melamine was extracted from the residue with water and purified by repeated recrystallisation. This substance is less diactinic than cyanuric acid, owing to the replacement of the three OH by three NH_2 groups. A layer 50 mm. in thickness of a solution containing 1 milligram-molecule in 40 c.c. of water transmitted all rays to $^1/\lambda$ 3638 (λ 2748).

Triethylmelamine (m. p. 74°).—The specimen examined was prepared by heating pure cyanuric chloride with excess of an alcoholic solution of ethylamine in a sealed tube at 100° for 6 hours. It was purified by crystallisation from dilute alcohol. As will be seen from the curve, its absorption is in close agreement with that of melamine. A solution of 1 milligram-molecule in 20 c.c. of alcohol transmits all rays to $^1/\lambda$ 3525 (λ 2836).

*Triethyliso*melamine.—The preparation of this substance in a state of purity was found to be most tedious and difficult. The method followed was that described by Hofmann (*Ber.*, 1869, 2, 452). The yield of mustard oil was very small; this was also Hofmann's experience. On the other hand, no difficulty was experienced in converting the ethyl mustard oil into monoethylthiourea, although, so far as could be ascertained, the method which we followed did not differ from that given by Hofmann. It was found also that little heat was evolved by the action of ammonia on the ethyl mustard oil, and that the solution, on evaporation, crystallised without difficulty. The melting point of the crystals differed by only 1° from that given by Hofmann. The desulphurisation of the ethylthiourea was effected by repeatedly boiling with freshly precipitated and carefully dried mercuric oxide until the oxide was no longer darkened. On filtering the solution and evaporating, a thick syrup was obtained which crystallised only after long standing and upon subsequent repeated treatment with solvents, notwithstanding that every precaution was taken, as recommended by Hofmann, to thoroughly purify and dry both the mercuric oxide and the alcohol. Details are given of the preparation of this substance, as it seems to have been but little investigated since the publication of Hofmann's paper.

The spectra of triethyl*iso*melamine show less absorption than melamine and triethylmelamine, in this respect they bear the same relation to those substances that ethyl *iso*cyanurate bears to cyanuric acid and ethyl cyanurate.

Notes on the Curves.—For an account of the method employed in drawing the curves on p. 854, see Trans., 1899, 75, 649, and the papers mentioned therein.

The thickness of the layer of liquid in millimetres is given in the

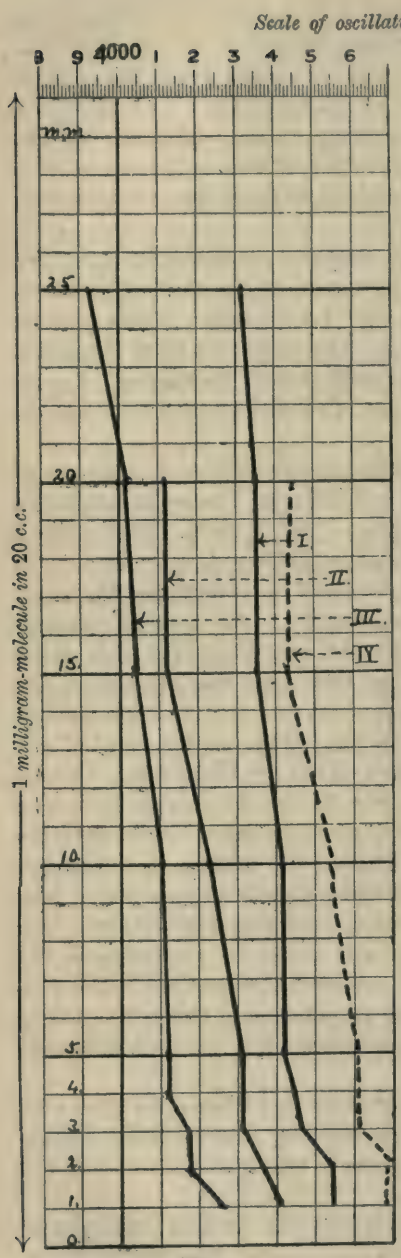


FIG. A.

I. Methyl *iso*cyanurate, m. p. 175°.
II. Cyanuric acid.
III. Methyl cyanurate, m. p. 135°.
IV. *Curve deduced for the hypothetical* iso*cyanuric acid.*

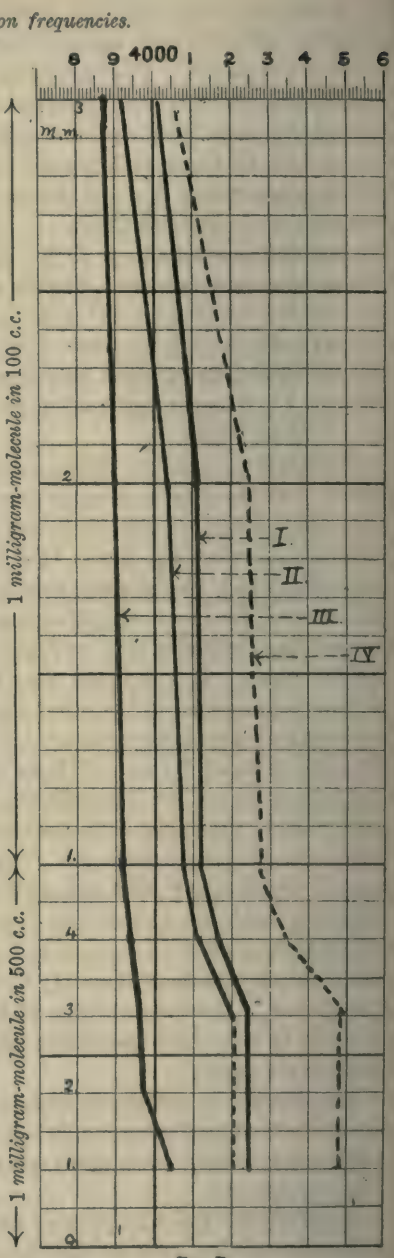


FIG. B.

I. Triethyl *iso*melamine, m. p. 92°.
II. Melamine.
III. Triethylmelamine, m. p. 74°.
IV. *Curve deduced for the hypothetical* iso*melamine.*

column headed 'mm.' on the left-hand side of each of the figures A and B.

In the case of cyanuric acid, 1 milligram-molecule was dissolved in 60 c.c. of water, and layers of 3—60 mm. in thickness were photographed. For the sake of easy comparison with the curves of the esters, 60 mm. of this solution are taken as equivalent to 20 mm. of a solution containing 1 milligram-molecule in 20 c.c., and the curve plotted accordingly.

The curves for the stronger solutions of melamine and triethylmelamine are not given, as we were unable to obtain photographs of the corresponding solutions of triethyl*iso*melamine for comparison.

The difference between the curves II and III (Fig. A) is due to the greater molecular weight of the ester, which contains three methyl groups in place of three hydrogen atoms, and therefore has greater absorption than the acid. The difference between curves I and III expresses the difference in the amount of absorption which is caused by the difference in constitution of the two esters. Assuming the relation between the unknown *iso*cyanuric acid and its alkyl derivative to be the same as that between the normal acid and its ester, the curve of *iso*cyanuric acid would be represented approximately by the dotted line IV. The difference in the amount of absorption due to the difference in constitution between the normal and the *iso*-acid would then be expressed by the difference between the curves II and IV.

The melamine curves (Fig. B) are to be interpreted in the same manner.

Potassium cyanate. N⋮C·OK or O:C:NK.

1 milligram-mol. in 4 c.c. water.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
50, 40, 30	Spectrum continuous to ..... Complete absorption beyond.	4128	2422
20, 10	Spectrum continuous to ..... Complete absorption beyond.	4325	2312
8, 6, 4	Spectrum continuous to ..... Complete absorption beyond.	4417	2263
2	Same as 4 mm., with lines showing faintly at	4484	2230
	and	4561	2192

Methyl iso*Cyanate*; *Methylcarbimide.* $CO{:}NH{\cdot}CH_3$. B. p. 44°.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
2	Spectrum continuous to	3638	2748
	But weak from	3462	2888
	to	3638	2748
	Complete absorption beyond.		
1	Spectrum continuous to	3638	2748
	Complete absorption beyond.		

Ethyl iso*Cyanate*; *Ethylcarbimide.* $CO{:}NH{\cdot}C_2H_5$. B. p. 60°.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
1	Spectrum continuous to	3638	2748
	Complete absorption beyond.		

Cyanuric Chloride. $C_3N_3Cl_3$. M. p. 146°.

1 milligram-mol. in 4 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
25	Spectrum continuous to	3315	3016
	Faint line at	3345	2989
	Complete absorption beyond.		
20, 15, 10	Spectrum continuous to	3345	2989
	Complete absorption beyond.		
5, 4	Spectrum continuous to	3482	2871
	Complete absorption beyond.		
3, 2	Spectrum continuous to	3516	2844

Cyanuric Chloride—(continued).

1 milligram-mol. in 20 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$.	λ.
25	Spectrum continuous to	3340	2994
	Complete absorption beyond.		
20	Spectrum continuous to	3438	2908
	Complete absorption beyond.		
15	Spectrum continuous to	3516	2844
	Complete absorption beyond.		
10	Spectrum continuous to	3559	2809
5	Complete absorption beyond.		
4	Spectrum continuous to	3628	2756
3			
2	Complete absorption beyond.		

Cyanuric Acid. $C_3N_3O_3H_3$.

Schuchardt's specimen recrystallised from water.

1 milligram-mol. in 60 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$.	λ.
60	Spectrum continuous to	3886	2573
	Weak prolongation to	4132	2420
	Complete absorption beyond.		
45	Spectrum continuous to	4132	2420
	Complete absorption beyond.		
30	Spectrum continuous to	4176	2394
	Faint prolongation to	4230	2364
	Complete absorption beyond.		
15	Spectrum continuous to	4321	2314
12			
9	Complete absorption beyond.		
6	Spectrum continuous to	4368	2289
	Complete absorption beyond.		
3	Spectrum continuous to	4417	2263
	Complete absorption beyond.		

Methyl Cyanurate, $C_3N_3(O\cdot CH_3)_3$. M. p. 134·5°.

1 milligram-mol. in 8 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
50	Spectrum continuous to	3807	2626
	Faint line at	3870	2583
	Complete absorption beyond.		
40	Spectrum continuous to	3870	2583
30	Complete absorption beyond.		
20	Spectrum continuous to	3911	2556
	Complete absorption beyond.		
10	Spectrum continuous to	4020	2487
8	Complete absorption beyond.		
6			
4	Spectrum continuous to	4112	2431
2	Complete absorption beyond.		

Methyl Cyanurate—(continued).

1 milligram-mol. in 20 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
25	Spectrum continuous to	3922	2549
20	Complete absorption beyond.		
15	Spectrum continuous to	4032	2480
	Complete absorption beyond.		
10	Same as 15 mm., but faint prolongation to	4112	2431
5	Spectrum continuous to	4125	2424
4	Complete absorption beyond.		
3	Spectrum continuous to	4176	2394
2	Complete absorption beyond.		
1	Spectrum continuous to	4245	2355
	Complete absorption beyond.		

Methyl iso*Cyanurate; Methyltricarbimide*, $C_3O_3(N{\cdot}CH_3)_3$. M. p. 175°.

1 milligram-mol. in 8 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
50	Spectrum continuous, but weak to	3313	3018
	Very faint indication of lines at.....	3480	2873
	and	3509	2849
	Complete absorption beyond.		
40	Spectrum continuous to.....	3555	2812
	Complete absorption beyond.		
30	Spectrum continuous to	3625	2758
	Complete absorption beyond.		
20	Same as 30 mm., very faint prolongation to.....	3873	2581
	And lines at	4102	2437
	and	4116	2429
	Complete absorption beyond.		
10, 8	Spectrum continuous to.....	4306	2322
	Complete absorption beyond.		
6, 4, 2	Spectrum continuous to	4402	2271
	Complete absorption beyond.		

Methyl iso*Cyanurate; Methyltricarbimide*—(continued).

1 milligram-mol. in 20 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
25	Spectrum continuous to	4321	2314
	Complete absorption beyond.		
20, 15	Spectrum continuous to	4368	2289
	Complete absorption beyond.		
10, 5	Spectrum continuous to.....	4413	2266
	Complete absorption beyond.		
4	Spectrum continuous to.....	4448	2248
	Complete absorption beyond.		
3	Substantially as above.		
	Complete absorption beyond.		
2	Spectrum continuous to	4560	2192
	Complete absorption beyond.		
1	Spectrum continuous to	4555	2195
	Complete absorption beyond.		

Ethyl iso*Cyanurate; Ethyltricarbimide.* $C_3O_3(N{\cdot}C_2H_5)_3$. M. p. 95°.

1 milligram-mol. in 20 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$.	λ
25	Spectrum continuous to	4105	2436
	Feeble transmission to	4335	2306
	Complete absorption beyond.		
20	Spectrum continuous to	4215	2372
	Feeble transmission to	4368	2280
	Complete absorption beyond.		
15	Spectrum continuous to	4335	2306
	Lines transmitted at	4347	2300
	and	4368	2289
	Complete absorption beyond.		
10	Spectrum continuous to	4347	2300
	Lines at	4368	2289
	and	4325	2312
	Complete absorption beyond.		
5, 4, 3	Spectrum continuous to	4325	2312
	Complete absorption beyond.		
2, 1	Spectrum continuous to	4507	2218
	Line at	4572	2187
	Complete absorption beyond.		

Melamine; Cyanurtriamide. $C_3N_3(NH_2)_3$.

1 milligram-mol. in 40 c.c. water.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$1/\lambda$.	λ.
50, 40, 30	Spectrum continuous to	3638	2748
	Complete absorption beyond.		
20	Spectrum continuous to	3648	2741
	Complete absorption beyond.		
10, 8	Spectrum continuous to	3667	2727
	Complete absorption beyond.		
6	Spectrum continuous to	3707	2697
	Complete absorption beyond.		
4	Spectrum continuous to	3740	2673
	Complete absorption beyond.		
2	Spectrum continuous to	3886	2573
	Complete absorption beyond.		

Melamine; Cyanurtriamide—(continued).

1 milligram-mol. in 100 c.c. water.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
5, 4	Spectrum continuous to	3877	2579
	Complete absorption beyond.		
3	Spectrum continuous to	3918	2552
	Complete absorption beyond.		
2	Spectrum continuous to	4038	2476
	Complete absorption beyond.		
1	Spectrum continuous to	4080	2450
	Complete absorption beyond.		

1 milligram-mol. in 500 c.c. water.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
5	Spectrum continuous to	4080	2450
	Feeble transmission to	4315	2314
	Complete absorption beyond.		
4	Spectrum continuous to	4125	2424
	Feeble transmission to	4362	2292
	Complete absorption beyond.		
3, 2, 1	Spectrum continuous to	4200	2380
	Feeble transmission to	4407	2269
	Complete absorption beyond.		

Triethylmelamine. $C_3N_3(NH\cdot CH_3)_3$ M. p. 74°.

1 milligram-mol. in 20 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
25	Spectrum continuous to	3525	2836
	Strong line transmitted at	3635	2751
	Complete absorption beyond.		
20, 15, 10	Spectrum continuous, but weak, to ...	3635	2751
	Complete absorption beyond.		
5, 4	Spectrum continuous to	3777	2647
	Complete absorption beyond.		
3	Spectrum continuous to	3812	2623
	Complete absorption beyond.		
2	Spectrum continuous to	3830	2610
	Strong line transmitted at	3886	2573
	Complete absorption beyond.		
1	Spectrum continuous to	3886	2573
	Complete absorption beyond.		

Triethylmelamine—(continued).
1 milligram-mol. in 100 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
5 } 4 }	Spectrum continuous to	3830	2610
	Strong line transmitted at	3886	2573
	Complete absorption beyond.		
3	Spectrum continuous to	3886	2573
	Complete absorption beyond.		
2	Spectrum continuous to	3901	2563
	Complete absorption beyond.		
1	Spectrum continuous to	3914	2554
	Complete absorption beyond.		

1 milligram-mol. in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
5	Spectrum continuous to	3914	2554
	Complete absorption beyond.		
4	Spectrum continuous to	3935	2541
	Complete absorption beyond.		
3	Spectrum continuous to	3967	2520
	Complete absorption beyond.		
2	Spectrum continuous to	3985	2509
	Complete absorption beyond.		
1	Spectrum continuous to	4043	2473
	Complete absorption beyond.		

Triethylisomelamine. $C_3N_3H_3(N{\cdot}C_2H_5)_3 + 4H_2O$. M. p. 92°.
1 milligram-mol. in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
20	Spectrum continuous to	3620	2762
	Line feebly transmitted at	3681	2716
	Complete absorption beyond.		
15	Spectrum continuous to	3805	2628
	Complete absorption beyond.		
10	Spectrum continuous to	3852	2596
	Complete absorption beyond.		
5	Spectrum continuous to	3911	2556
	Complete absorption beyond.		
4	Spectrum continuous to	3988	2507
	Complete absorption beyond.		
3	Spectrum continuous to	4023	2485
	Complete absorption beyond.		
2	Spectrum continuous to	4116	2429
	Complete absorption beyond.		

Triethylisomelamine—(continued).

1 milligram-mol. in 500 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
5	Spectrum continuous to	4116	2429
	Complete absorption beyond.		
4	Spectrum continuous to	4165	2400
	Complete absorption beyond.		
3	Spectrum continuous to	4165	2400
	Faint line at	4234	2361
	Complete absorption beyond.		
2	Spectrum continuous to	4234	2361
	Complete absorption beyond.		

XCII.—*A New Method for the Determination of Hydrolytic Dissociation.*

By Robert Crosbie Farmer, B.Sc. (Vict.), Ph.D. (Würzburg), Priestley Scholar in the University of Birmingham.

It is well known that salts of weak acids or weak bases are partially dissociated in aqueous solution into free acid and base. This is due to the fact that water is to a slight extent ionised, and is therefore capable of acting at the same time as a weak acid and a weak base. In many cases, it becomes a matter of importance to determine to what extent this hydrolytic dissociation takes place.

Walker has recently shown (*Zeit. physikal. Chem.*, 32, 1900, 137) that the relation between the dissociation constant of an acid, and the hydrolysis of its salts may be expressed mathematically, and that if the dissociation constant for pure water is known, the hydrolysis of a salt may be calculated from the conductivity of the corresponding acid or base, and *vice versâ*. For this reason, a more complete study of hydrolytic dissociation seems desirable.

Of the methods at present in use for the determination of hydrolysis, the chief ones are (Ley, *Zeit. physikal. Chem.*, 1899, 30, 193),

(i) The determination of the electric conductivity of the salt in question at different dilutions.

(ii) The measurement of the free acid or alkali present in the system by the velocity of hydrolysis of esters, or of the inversion of sugar by a solution of the salt.

Of these, the former can scarcely claim anything more than a qualitative significance. It is known for instance, that in the case of all sodium salts which are not hydrolysed in aqueous solution, the difference between the molecular conductivity at the dilution $v = 32$

litres, and that at $v = 1024$ litres approximates to 10 units. If the salt is hydrolysed, this difference will exceed 10 units, the higher conductivity at the dilution $v = 1024$ litres, being due to the excess of sodium hydroxide which is set free from the salt by the water.

This method is, however, neither sensitive nor exact, and so far no attempt appears to have been made to calculate the extent of the hydrolysis from the increase of the conductivity with the dilution. The method of determining the amount of free acid or base by the velocity of hydrolysis has, on the other hand, been used with considerable success. With the aid of a somewhat complicated formula, Shields (*Zeit. physikal. Chem.*, 1893, 12, 167) has applied the method to the measurement of hydrolysis in the case of the salts of weak acids, such as phenol, &c. Still, there are certain cases in which Shields' method becomes inapplicable, and it is with the view of supplying this deficiency that the following method was devised.

If we attempt to apply the method described by Shields to the determination of the hydrolysis of a salt whose acid is sparingly soluble in water, we are met with the difficulty that the free acid begins to separate out from the solution before the reaction has proceeded very far. The equilibrium of the system is thereby upset, and the formula for the calculation of the results ceases to hold. It also occasionally happens, in working with unstable substances, that the acid decomposes during the progress of the hydrolysis, especially if the latter requires several days for its completion up to a point where accurate results may be deduced from it. This was found to be the case, for instance, when the attempt was made to determine the hydrolysis of sodium nitrosophenolate (Farmer and Hantzsch, *Ber.*, 1899, 32, 3106). To overcome these difficulties, advantage has been taken of the fact that a substance distributes itself between two immiscible solvents in a constant ratio, independent of the dilution, that is, if we except the case of substances which exist in one of the two solvents in a state of abnormal molecular aggregation. The determinations are easy to carry out and involve much simpler calculations than the last-mentioned method.

The substance used in the following experiments was one to which Shields' method was inapplicable, owing to its sparing solubility in water, namely, hydroxyazobenzene. If an aqueous solution of a salt of hydroxyazobenzene is shaken with benzene, some free hydroxyazobenzene is taken up by the benzene layer. From the quantity of hydroxyazobenzene thus extracted, it is possible to calculate to what extent the salt is hydrolysed in aqueous solution.

It is first necessary to determine the coefficient of distribution for hydroxyazobenzene between benzene and water. To determine the solubility of hydroxyazobenzene in benzene, a certain quantity of a saturated solution was evaporated down and the residue weighed. Owing to

its volatility at 100°, the hydroxyazobenzene could only be slightly warmed during the evaporation (which was accelerated by a current of air), and was then dried in a desiccator until the weight was constant. To determine its solubility in water, the usual method of evaporation could not be used, owing to the volatility of the hydroxyazobenzene. The most convenient method was to extract the hydroxyazobenzene from the aqueous solution with ether, and evaporate down the ethereal extract. On account of the great solubility of hydroxyazobenzene in ether, it was quite sufficient to extract the aqueous solution twice.

The residue from the ether was dried in a desiccator as before and weighed. The dried hydroxyazobenzene showed no traces of volatility on continued standing over sulphuric acid in a desiccator at the ordinary temperature.

In the carrying out of the distribution experiments, we have not to do with pure benzene and water, but with mutually saturated solutions of the two solvents. The solubility determinations were therefore also carried out with benzene containing water and with water containing benzene.

For the solubility of hydroxyazobenzene in water at 25°, the following values were obtained :

Solubility of hydroxyazobenzene in pure water free from carbon dioxide. Temp. 25°.

(i) 1000 c.c. of the solution gave 0·0227 gram hydroxyazobenzene.
(ii) 1000 „ „ 0·0223 „ „

Solubility in water containing benzene.

(i) 1000 c.c. of the solution gave 0·0268 gram hydroxyazobenzene.
(ii) 1000 „ „ 0·0265 „ „
(iii) 500 „ „ 0·0159 „ „
Mean = **0·0284** „ per litre.

Solubility in benzene containing water. Temp. 25°.

Ten c.c. of saturated solutions gave successively 0·1525, 0·1524, 0·1508, 0·1513, 0·1524, and 0·1528 gram of residue. Mean = **0·1520** gram in 10 c.c.

This gives as the ratio of solubilities

$$\frac{0{\cdot}1520 \times 1000}{0{\cdot}0284 \times 10} = 535.$$

This was confirmed by distributing between water and benzene a quantity of hydroxyazobenzene insufficient to saturate the two solvents.

Distribution of hydroxyazobenzene between benzene and water. Temp. 25°.

	Hydroxyazobenzene from 1000 c.c. of the aqueous solution.	Hydroxyazobenzene from 10 c.c. of the benzene solution.	Coefficient of Distribution.
i.	0·0198	0·1125	568
ii.	0·0198	0·1025	518
iii.	0·0217	0·1135	523
iv.	0·0199	0·1096	551
v.	0·0215	0·1152	536
		Mean =	**539**

The mean of these values, namely, 539, was taken as the true coefficient of distribution in the following experiments.

In the determination of the hydrolysis, the barium salt of hydroxyazobenzene was used, as it is almost impossible to prepare a caustic soda solution absolutely free from carbonate.

A weighed quantity of hydroxyazobenzene was brought into a large stoppered bottle of about 1400 c.c. capacity and a known quantity of benzene added. In the following experiments, 60 c.c. of benzene were taken. A solution of barium hydroxide in 1000 c.c. of water was then added, and the whole brought to 25° in a thermostat. Hereupon, the benzene and water were well mixed by shaking, and again allowed to stand in the thermostat until the two layers had completely separated. The water was then syphoned off and 50 c.c. of the benzene removed by means of a pipette. The benzene solution was evaporated down, and the residue dried in a desiccator until of constant weight.

As the solubility of benzene in water is very slight, it was not considered necessary to make allowances for the small changes in volume in calculating the concentrations of the solutions.

Calculation of the Results.

The coefficient of distribution for hydroxyazobenzene between benzene and water was found to be 539, that is, benzene always takes up 539 times as much hydroxyazobenzene as water, if the two solvents are present in equal volumes. We will designate this coefficient by F. If the two solvents are present in unequal quantity, say 1 litre of water to q litres of benzene, the hydroxyazobenzene will distribute itself between them in the ratio $1 : qF$.

If we take a solution of hydroxyazobenzene in baryta water and shake it with benzene, the benzene will extract free hydroxyazobenzene from the barium salt until the two following equilibria have adjusted themselves.

i. $C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH + baOH \rightleftarrows C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}Oba + H{\cdot}OH.$
ii. Hydroxyazobenzene in water $\rightleftarrows$ Hydroxyazobenzene in benzene.

From the quantity of hydroxyazobenzene taken up by the benzene, the degree of hydrolysis can be calculated as follows.

Let the concentration of the hydroxyazobenzene in the aqueous solution be c_2 gram equivalents per litre, and that of the barium hydroxide c_1 equivalents per litre. For each litre of water we take, as above, q litres of benzene. After equilibrium has been reached, a certain quantity of the benzene is removed by a pipette, filtered, and evaporated. The residue is weighed, and from its weight the quantity of hydroxyazobenzene in the whole 60 c.c. is calculated. We can calculate from this, by multiplying by $1/qF$, how much free hydroxyazobenzene is present in the aqueous solution. This quantity must be expressed in gram equivalents per litre. We will call this concentration c.

The following quantities are therefore known :

c_2 = Original concentration of hydroxyazobenzene.
c_1 = „ „ barium hydroxide.
c = Concentration of free hydroxyazobenzene in the water after shaking up with benzene.

For the equilibrium :

$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH + baOH \rightleftarrows C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}Oba + H{\cdot}OH,$

we have the equation $m_1d_1 \times m_2d_2 = m_3d_3 \times m_4d_4$, where m_1, m_2, m_3, and m_4 are the concentrations, and d_1, d_2, d_3, and d_4 are the degrees of dissociation of the four substances. It has been shown (Arrhenius, *Zeit. physikal. Chem.*, 1890, **5**, 17) that this equation may be simplified so as to read

$$m_1m_2 = km_3m_4.$$

We have now :

m_1 = Concentration of the free hydroxyazobenzene in the water = c.

If this quantity is c, a corresponding quantity, cqF, must have been taken up by the benzene. The total quantity of free hydroxyazobenzene is therefore c (in the water) $+ cqF$ (in the benzene). Total = $c(1+qF)$.

The remainder of the hydroxyazobenzene is present in the form of its barium salt. The concentration of the barium salt which has escaped hydrolysis is therefore $c_2 - c(1+qF)$.

$$m_3 = c_2 - c(1+qF).$$

The total concentration of baryta is c_1. Of this, part is free and part is combined as barium salt. The quantity of barium salt is m_3; the quantity of free barium hydroxide is therefore equal to $c_1 - m_3$, that is,

$$m_2 = c_1 - c_2 + c(1+qF).$$

m_4 = Concentration of the water. This is practically constant. Consequently, km_4 is also constant.

The equation $m_1m_2 = km_3m_4$ must therefore be written:

$$c\{c_1 - c_2 + c(1+qF)\} = km_4\{c_2 - c(1+qF)\},$$

or

$$km_4 = \frac{c\{c_1 - c_2 + c(1+qF)\}}{c_2 - c(1+qF)}. \quad . \quad . \quad . \quad . \quad (i)$$

From this equation, km_4 can be calculated.

Let us now consider the normal system,

$$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH + baOH \rightleftarrows C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}Oba + H{\cdot}OH,$$

in absence of benzene and without any excess of baryta. We have the condition

$$m_1m_2 = km_3m_4.$$

In this case, however, it is evident that $m_1 = m_2$ and $m_3 = c_2 - m_1$. Consequently,

$$m_1^2 = km_4(c_2 - m_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

From this equation, m_1 can be calculated.

Finally, the degree of hydrolysis $= \frac{m_1}{c_2}$

and the percentage hydrolysis $= \frac{100m_1}{c_2}$. . . . . (iii)

The carbon dioxide of the air must of course be excluded as rigidly as possible. It has the effect of setting free too much hydroxyazobenzene and thus giving values which are too high. This effect shows itself most strongly when approximately equivalent quantities of hydroxyazobenzene and barium hydroxide are taken. It may, however, be almost completely avoided by using excess of barium hydroxide, so that the quantity of carbon dioxide which finds its way into the solution is small in comparison with the total amount of free alkali present. For instance, by taking different excesses of barium hydroxide, the following values were obtained.

Concentration = $N/64$. Temp. = 25°.

Excess of barium hydroxide, approx.	− 5	0	10	20	per cent.
Percentage of hydrolysis (found) ...	1·45	1·34	1·26	1·21	„

Concentration = $N/100$. Temp. = 25°.

Excess of barium hydroxide, approx.	0	11	20	94	per cent.
Percentage of hydrolysis (found) ...	2·36	1·80	1·55	1·65	„

In the case of hydroxyazobenzene it is advisable to use an excess of baryta amounting to 10 to 20 per cent. Thus, the error due to carbon dioxide is reduced to a minimum, and the quantities of

Summary of Experiments.

FIRST SERIES. *Dilution* = 100 *litres.* *Temp.* = 25°.

	Volume of water in c.c.	Volume of benzene in c.c.	Original concentration of hydroxyazobenzene. c_2.	Original concentration of $Ba(OH)_2$. c_1.	Residue from 50 c.c. benzene in gram.	Calculated concentration of the free hydroxyazobenzene in the water. c.	$\frac{c[c_1 - c_2 + c(1+qF)]}{c_2 - c(1+qF)} = km_1$.	m_1 from equation ii.	$\frac{m_1}{c_2}$. Equation iii.	Percentage hydrolysis.
i	1000	60	0·00998	0·01002	0·2027	0·00003795	$10^{-6} \times 5·71$	0·000236	0·0236	2·36
ii	1000	60	0·01000	0·01113	0·0954	0·00001788	$10^{-6} \times 3·29$	0·000180	0·0180	1·80
iii	1000	60	0·01000	0·01201	0·0537	0·00001006	$10^{-6} \times 2·45$	0·000155	0·0155	1·55
iv	1000	60	0·01000	0·01941	0·0153	0·00000287	$10^{-6} \times 2·75$	0·000165	0·0165	1·65
SECOND SERIES. *Dilution* = 64 *litres.* *Temp.* = 25°.										
i	500	60	0·01562	0·01494	0·1695	0·00003176	$10^{-6} \times 3·31$	0·000226	0·0145	1·45
ii	500	60	0·01560	0·01567	0·1287	0·00002408	$10^{-6} \times 2·83$	0·000209	0·0134	1·34
iii	1000	60	0·01564	0·01717	0·0950	0·00001780	$10^{-6} \times 2·51$	0·000197	0·0126	1·26
iv	1000	60	0·01559	0·01872	0·0543	0 00001018	$10^{-6} \times 2·32$	0·000189	0·0121	1·21
THIRD SERIES. *Dilution* = 80 *litres.* *Temp.* = 25°.										
i	1000	60	0·01250	0·01389	0·0771	0·00001445	$10^{-6} \times 2·25$	0·000166	0·0133	1·33
ii	1000	60	0·01249	0·01461	0·0574	0·00001076	$10^{-6} \times 2·21$	0·000165	0·0132	1·32
FOURTH SERIES. *Dilution* = 50 *litres.* *Temp.* = 25°.										
i	1000	60	0·02002	0·02201	0·0939	0·00001760	$10^{-6} \times 2·34$	0·000215	0·0107	1·07
ii	1000	60	0·02000	0·02413	0·0569	0·00001066	$10^{-6} \times 2·44$	0·000220	0·0110	1·10
FIFTH SERIES. *Dilution* = 32 *litres.* *Temp.* = 25°.										
i	1000	60	0·03125	0·02974	0·3982	0·00007462	$10^{-6} \times 2·54$	0·000281	0·0090	0·90
ii	500	60	0·03125	0·03438	0·0987	0·00001850	$10^{-6} \times 2·68$	0·000288	0·0092	0·92

hydroxyazobenzene in the benzene extract are still sufficiently large to be easily weighed.

The effect of dilution on the hydrolysis is expressed, as has been shown by Arrhenius, by the equation $x^2/(1 - x)v$ = const., where x = degree of hydrolysis, and v = dilution. If we omit the results which were, as above shown, most affected by the action of carbon dioxide, we obtain the following

Table of results.

Dilution.	Percentage of hydrolysis.	$x^2/(1 - x)v$ = const.
32	0·90	25×10^{-7}
32	0·92	26 „
50	1·07	23 „
50	1·10	24 „
64	1·26	25 „
64	1·21	23 „
80	1·33	22 „
80	1·32	22 „
100	1·55	25 „
100	1·65	28 „
	Mean	24·3 „

According to Walker (*Zeit. physikal. Chem.*, 1900, 32, 137), the dissociation constant of an acid may be calculated from the hydrolysis of its salts. If x is the degree of hydrolysis and k the dissociation constant, we have the relation,

$$\frac{x^2}{(1 - x)v} = \frac{(1{\cdot}09 \times 10^{-7})^2}{k}.$$

This would give a dissociation constant for hydroxyazobenzene of $4{\cdot}9 \times 10^{-9}$. A discussion as to the bearing of this on the question of the constitution of the hydroxyazo-bodies must be postponed until more accurate measurements of the electric conductivity of hydroxyazobenzene have been made. The present paper is concerned only with the application of the method of distribution to the determination of hydrolysis. In most cases, it would probably be advantageous to determine the amounts of acid by titration instead of gravimetrically. This was inapplicable in the case of hydroxyazobenzene, on account of the intense colour of the solutions. The method of distribution is of course as well adapted to the investigation of the salts of weak bases as to that of the salts of weak acids.

CHEMICAL LABORATORIES,
UNIVERSITY OF BIRMINGHAM.

ANNUAL GENERAL MEETING,

March 28th, 1901.

Professor T. E. Thorpe, C.B., LL.D., F.R.S., President, in the Chair.

The following Report was read by the President:—

The Chemical Society was founded about four years after the accession to the Throne of the Gracious Lady whose recent loss we deplore, and the memory of whose virtues and worth, as a woman and as a monarch, will for ever abide with us. We are proud to think that this Society, in so far as it has ministered to the progress of chemistry, may have contributed in some measure to the lustre of a reign which has been pre-eminently associated with the development and spread of science in this country, and with the extension of those arts which rest upon chemistry. We have never been unmindful of what our science owes to the Royal Family, and in particular to the late Prince Consort, whose appreciative interest in the fortunes of the Royal College of Chemistry, of which he was the President, and whose friendship for the eminent man who made it the first organised school of chemical research in this country, has directly ministered to the activity, welfare, and usefulness of our Society. We sought to give utterance to these sentiments in an Address which we ventured to submit to His Majesty on his accession to the Throne, and in respectfully tendering our congratulations, and in offering our homage, we expressed the hope that his reign might be marked by discoveries in the science we represent not less brilliant than those which have characterised the reign of his illustrious mother.

We enter upon the twentieth century mustering 2370 members, made up as follows:

Number of ordinary Fellows on March 29th, 1900 ...		2292
„ „ reinstated by Council ...		5
„ „ since elected		117
Withdrawn	31	
Removed on account of non-payment of arrears ...	26	
Deceased	20	
	77	
Number of ordinary Fellows on March 28th, 1901 ...		2337
„ Foreign Fellows „ „ „ ...		33
		2370

Since the last anniversary the following have withdrawn:—E. L. Allhusen; J. Allport; Frank Bastow; F. Barker Cooke; G. H. Cross; Sir Michael Foster; J. Frost; H. E. Gardner; J. F. H. Gilbard; William Goddard; Frederic Gothard; Robert Hamilton; Harold Ellershaw Head; William M. Heller; Henry Leonard Hinnell; Alfred Kingsby Howard; Edgar Joseph; A. E. Lewis; C. T. Macadam; Fred Marsden; James Maso; John Charles Platts; Percy Morrice Randall; S. G. Rosenblum; Edward Rosling; James Spencer; James H. Stebbins; Sydney Steel; William Ward; A. Swainson Waterfield; P. A. Wier.

The names of those removed were:—Carl Bennert; G. F. Brindley; R. E. Brown; James Crowther; W. B. Edwards; Sidney Fawns; D. A. Griffiths; W. T. Gronow; R. Glode Guyer; W. G. Lasseter; H. E. Law; J. A. MacFarlane; Angus Mackay; E. MacSwiney; S. M. Martin; Robert McClumpha; W. B. McVey; E. E. Milnes; H. J. Monson; R. H. Owen; J. B. Reid; H. J. Phillips; James Speakman; Thomas Stormouth; J. B. Thornley; H. W. Wallis; A. W. Warwick; R. H. Wilson.

The names of the deceased Fellows are:—Edmund Atkinson; John Borland; Alfred Hunter Boylan; William Harcourt Branscombe; Sir John Conroy; Henry Howard Crawley; Thomas Flower Ellis; Frank W. Harris; Herbert A. Hotblack; Sir John Bennet Lawes; Stevenson Macadam; Frederick Alfred Manning; William McConnell; William Parsons; Richard Reynolds; Saville Shaw; George Smith; C. J. H. Warden; Augustus A. Wood; Thomas M. Wyatt.

In Edmund Atkinson we have lost a fellow of marked individuality, a strong and vigorous personality, the memory of whose genial presence, sturdy common sense, and mordant yet kindly humour those of us who knew him will not willingly let die. He is best known, of course, as a physicist, as the editor of a popular text-book of physics, and as an officer of the Physical Society. But he began his scientific career as a chemist, studying under Bunsen and Wöhler, and working on glycol and on lophine. He joined our Society in 1859, was a member of the Council in 1868—1871, in 1882—1885, in 1891—1892, and became a Vice-President in 1893—1896. A more extended notice of his life and works will be contributed to our Journal by his life-long friends, Professor Carey Foster and Dr. Hugo Müller.

By the death of Lieutenant Thomas Flower Ellis we have lost a young metallurgical chemist of considerable promise, of great personal charm, beloved by all who learned to know his frank and manly nature. He passed through the Chemical Courses of the Royal College of Science, working for a time in the research laboratory under my direction. After spending some years at the

Straits Trading Company's Tin Smelting Works, at Pulo Brani, as an assayer, he went to South Africa as a mining engineer, and at the outbreak of hostilities joined Thorneycroft's Mounted Infantry, and was mortally wounded at the disastrous reverse of Spion Kop. With what courage and hardihood he faced that terrible ordeal, and how he met his end, has been told by Mr. Oppenheim in the January number of this year's *Nineteenth Century and After*.

Sir John Bennet Lawes, at the time of his death, had completed fifty years of membership of our body. His name is inseparably connected with that of his life-long friend and coadjutor, our veteran President—Sir Henry Gilbert, the father of the Society—in the development of scientific agriculture in this country, more especially in the famous field experiments at his ancestral home of Rothamsted. Sir John Lawes served on the Council in 1862—1865, and much of the outcome of the experimental inquiries which we owe to his broad-minded munificence is to be found in the pages of our Transactions.

We hope to have a fuller account of Sir John Lawes's life-work from the pen of Professor Warington.

Richard Reynolds, a former Lecturer in Chemistry at the Leeds School of Medicine, now incorporated within the Yorkshire College—a constituent college of the Victoria University—who died on April 5th, 1900, at the age of 70, was a man who deserves to be had in remembrance, not only as a representative pharmacist, singularly well cultured and strenuously active in all that concerned the best and truest interests of his calling, but as the type of a good citizen whose highest ambition was to do what in him lay to further the social and intellectual welfare of the community with which his lot was cast. Born in Banbury, of Quaker parents, he went to Leeds in 1844 as an apprentice to the late Thomas Harvey, also a member of the Society of Friends, and a well-known citizen of that town, where his memory is still cherished as a man of rectitude, zealous and active in everything relating to the public good. The firm, which ultimately became known as Harvey and Reynolds, was originally established by William West, also a Quaker, a Fellow of the Royal Society, and an original Fellow of this Society, who published a number of analyses of Yorkshire mineral springs, and who preceded Reynolds as Lecturer in the Leeds Medical School. Reynolds, also like West, became one of the secretaries of the Leeds Philosophical Society, and both were presidents of the Pharmaceutical Conference. Reynolds, in fact, was one of the founders of the Conference, and acted as Honorary Secretary until 1871. He also took an active part

in the work of the Yorkshire Geological Society, and served for some years on its Council. He was, too, one of the founders of the Priestley Club in Leeds, a constant attendant at its meetings, and an occasional contributor—his communications having invariably a note of interest, expressed with a fastidious neatness and precision of statement eminently characteristic of the man. Most of his published work appeared in the *Pharmaceutical Journal*, in the *Reports* of the British Association, and in the *Proceedings of the Yorkshire Geological Society*. He joined our Society in 1857.

Richard Reynolds will be mainly remembered for the share he took, in conjunction with the late Lord Frederick Cavendish and Dr. Heaton, of Leeds, in establishing the Yorkshire College, now one of the most important and most successful of the provincial colleges founded upon the type of Owens College, Manchester. Richard Reynolds may be said to have dedicated his life to this work. He pursued it with a tenacity of purpose and an untiring zeal which no amount of opposition or discouragement could damp. To a quiet and somewhat reticent manner he added the saving grace of a sense of humour; he was an excellent observer, and a good judge of men. Although not a Yorkshireman by birth, he thoroughly understood, and was quick to recognise and appreciate, the sterling qualities of shrewdness, directness of purpose, and strong common sense which characterise the people with whom he identified himself. It was this intelligent sympathy, combined with a singular transparency of motive, an obvious unselfishness, and a simple, earnest manner, that, by compelling confidence, constituted the secret of his influence among the men with whom he worked. He was satisfied, however, to exercise his power in a quiet, unobtrusive way; platform appearances and public display were utterly uncongenial to him; self-seeking or anything approaching to ostentation was absolutely foreign to his nature. It is owing to the circumstance that I knew him to be quite unmindful of his own fame, content indeed with the *mens sibi conscia recti*, that I desire now to add my meed of appreciation of the man and of the work which he achieved. I lived with him through the struggling infancy of the College, with which we both were associated, he as Honorary Secretary to its Council, and I as its first teacher of Chemistry. I should be wanting in common gratitude if I neglected this opportunity of stating how much I owe to his broad and intelligent sympathy with the objects of my chair—a sympathy springing, no doubt, in part from his old association with the work of a teacher of chemistry, but, and in no less measure, also to his inherent love of the science. His quiet trust, his courage, his resourcefulness,

never failed even at the most critical juncture in the early history of the College. Although naturally wary, cautious even to a degree, he could be bold on occasion, and seize with an unerring instinct the psychological moment which made for success, and carry with him coadjutors who had learned to trust the soundness of his judgment, and to put their confidence in his instinctive recognition of expediency and right. What the Yorkshire College has now become is largely due to the character which he and those who worked with him impressed upon it in the first years of its existence, and their names deserve to be writ in imperishable letters upon its chief corner-stone.

Men with the civic virtues of Richard Reynolds are the highest ornaments of the State. We see their monuments in the number of rapidly developing places which, like Owens College and the Yorkshire College, adorn our towns and cities—colleges which have moulded, and are destined to mould still more profoundly, the intellectual features of our social and industrial life.

Saville Shaw, the honorary local secretary and treasurer of the Newcastle Section of the Society of Chemical Industry, died on November 5th, 1900, in the 36th year of his age. He was born at Ardwick, Manchester, and in 1880 went to Owens College, and eventually became an assistant in Sir Henry Roscoe's laboratory. In 1884 he was elected to a Demonstratorship in Chemistry in the Durham College of Science, Newcastle-on-Tyne, and was made Lecturer on Metallurgy and Assaying. He did a considerable amount of extension lecturing throughout the counties of Northumberland and Durham, and in recognition of his services was given the degree of M.Sc. by the University of Durham. He was a member of various committees of the North of England Institution of Mining and Mechanical Engineers, for whom he carried out several experimental investigations, particularly on matters connected with flameless explosives, and on the microstructure of metals and alloys. In 1883, he communicated to us a paper on the preparation of the pentathionates, in which he established the existence of these salts, in opposition to the statement of Spring, who had impugned the accuracy of Prof. Lewes' observations published in our Journal. He was elected into the Society in 1890.

On the last anniversary, it was my melancholy duty to have to chronicle the loss of an unusually large proportion of our limited number of honorary foreign members. I am pleased to have to report on this occasion that Death has stayed his hand for a while, and that the number of our foreign Fellows remains the same as at this time last year, namely, 33.

I have the pleasure to offer, on behalf of the Society, our warm congratulations to our former President and Treasurer, Dr. Russell, on the attainment, this year, of his Jubilee as a Fellow of our body. Dr. Russell, we are glad to see, wears his years so lightly that it will be news, I am sure, to most of the Fellows to learn that he was elected into the Society so far back as the epoch of the Great Exhibition, within ten years, in fact, of its foundation. He has lately, as we know, renewed his youth, and we may confidently hope that he will continue to cultivate, with unabated ardour, those congenial inquiries which the calls of office, and of professional duty, left him but little leisure to pursue.

Mr. Nevil Story Maskelyne, late Professor of Mineralogy in the University of Oxford, sometime Keeper of the Minerals in the British Museum, and a former Vice-President of this Society, also attains his Jubilee as a Fellow this year. I beg to offer him our congratulations on this event, and to express the hope that he may speedily recover from the illness with which he has recently been attacked.

Sir David Gamble, C.B., a well-known leader of chemical industry in South Lancashire, and Mr. Edward Riley, the veteran analyst, who served on the Council in 1878—1879, and was a frequent contributor to our Journal, more particularly on subjects connected with the metallurgy of iron, are also to be congratulated on reaching, this year, the fiftieth anniversary of their election into the Society.

In the early part of this year, our Foreign Secretary had the pleasure of tendering, by direction of the Council, our felicitations to our eminent Foreign Member, Professor Wladimir Markownikoff, of the University of Moscow, on the occasion of the commemoration of the 40th year of his Doctorate. Courtesies like these add to the comity of nations and serve to show that whatever political or racial divisions may separate people, men of science are linked together in a common brotherhood.

Since the last Anniversary, 182 communications have been made to the Society, as against 175 on the last occasion. This number is greater than we have had in any preceding year. In character and variety, the last year's communications will, I think, compare favourably with those of any previous session. Abstracts of all have appeared in the Proceedings, and 106 have already been published in the Transactions. The volume of Transactions for 1900 contains 127 memoirs, occupying 1210 pages; in the preceding year 120 papers were published, occupying 1166 pages. Of the 127 memoirs, 19 were concerned with General and Physical Chemistry, 17 with Inorganic Chemistry, 84 with Organic Chemistry, 6 with Analytical Chemistry, and 1 with Mineralogical Chemistry. Papers on Physiological Chemistry or on the Chemistry of Vegetable Physiology and Agricul-

ture are comparatively seldom brought before our Society, and not a single communication on these departments of science appears in the Journal of last year.

I ventured on the last occasion to impress upon contributors the wisdom of condensation; if brevity is the soul of wit, diffuseness is no less the bane of science. The profit with which one reads a contribution is not always in direct proportion to its length. It is a remarkable fact that memoirs which have been, as it were, points of departure in the history of our science, such, for example, as Cavendish's famous paper on the synthesis of water, Davy's papers on the discovery of potassium and on the nature of chlorine, Williamson on etherification, have occupied only a few pages of printed matter. The list of famous memoirs of which the same may be said might be greatly extended. You have only to glance at the publications of the Alembic Club, or at Ostwald's reprints of Chemical Classics, to see how tersely all that we esteem best in our literature has been expressed.

The character of our published work is, of course, the true index of our usefulness, and we have a just pride in the regard which is everywhere paid to our Journal. But to those who are entrusted with the management of the affairs of the Society the steadily increasing mass of literature to be dealt with is a subject of no little concern. The cost of publication is increasing even more rapidly than the increase of matter to be published, and each year sees an addition to the expenses on account of the Journal and Proceedings in the Treasurer's Balance Sheet, with no proportionate increase in the income of the Society. We trust, therefore, that contributors may bear these facts in mind, and extend their sympathy towards that most hardly worked of all our Committees—the Publication Committee. Its methods may at times appear draconian, but, after all, we must, to use the homely phrase, cut our coat according to our cloth. Those coats are not necessarily the best cut which contain a superfluity of cloth.

The volumes for 1900 contain 3758 abstracts of papers, published mainly in continental journals, occupying 1492 pages. Although the number of abstracts dealt with is 141 more than in the preceding year, which in its turn was nearly 800 more than in 1898, the space occupied is less by 300 pages than last year. I venture to think that the character of the abstracts as faithful *résumés* of contemporary chemical literature has in no wise suffered from the condensation to which they have been subjected.

The abstracts may be classified as follows :—

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry	712	1355

PART II.

General and Physical Chemistry		467
Inorganic Chemistry		383
Mineralogical Chemistry		174
Physiological Chemistry		336
Chemistry of Vegetable Physiology and Agriculture		368
Analytical Chemistry		675
	780	2403
Total in Parts I. and II.	1492	3758

I am sure, too, the Fellows must have noted with satisfaction the unvarying regularity with which the Journal now makes its appearance with the beginning of the month.

I am also able to congratulate the Society on the more prompt appearance of the Annual Index. For some years past the annual volumes have been indexed by a special staff under the direction of the Sub-Editor, but after the work of compiling the Collective Index, extending from 1873 to 1892, was finished, the Index Committee suggested to the Council the propriety of entrusting the duty of preparing the Annual Index to one person, who should be responsible, under the direction of the Editor, for its speedy publication. Mrs. Dougal, who compiled the Collective Index, has, at the request of the Council, taken charge of this work, and the new Index has, I trust, now reached the Fellows. Although this degree of promptitude compares very favourably with that obtained under the former system, we have reason to hope, from the experience of the last twelve months, that it may be possible, by a fresh arrangement with our printers, to issue the Annual Index within six or eight weeks after the completion of the year to which it relates.

In addition to the 127 memoirs, the volume for 1900 contains no fewer than four Memorial Lectures on the life-work of distinguished Foreign Members, namely, Victor Meyer, Bunsen, Friedel, and Nilson. In the January number of the present volume appears the admirable account of Rammelsberg's life and labours, which we owe to Professor Miers. The Society has now accumulated a considerable number—in

all 13—of these monographs of the work of eminent Fellows of this Society—men who have been largely instrumental in moulding the chemistry of the last half-century. Among them are masters of determinative chemistry, Stas, Bunsen, Marignac, Nilson, and Rammelsberg; leaders in organic chemistry, Hofmann, Kekulé, Victor Meyer, and Friedel; Pasteur, the greatest of biological chemists; distinguished workers in the borderland connecting physics and chemistry, Kopp and Helmholtz; and Lothar Meyer, historian and systematist. Now that the end of the century has been reached, the Council has determined to put together these memoirs, and to issue them, as indeed was intended from the outset, in a separate volume. The whole work will constitute a most interesting record of the personal history of chemical science during the last half-century. It forms, too, a worthy monument to those whom we seek to commemorate, and a token of our gratitude for the services which they have rendered to humanity.

The mention of the name of Helmholtz recalls to our minds the graceful and eloquent tribute which was paid to the genius and labours of that eminent man in this room by one whose voice is now for ever hushed. Fitzgerald was not of our number, but with that frank and ready courtesy so characteristic of his generous nature, he promptly responded to our invitation to act as the exponent of our homage to the memory of the great philosopher who, in that never-to-be-forgotten lecture of 1881, had himself testified before this Society, and in one of the most remarkable gatherings of which I have personal knowledge, to the feeling with which the whole civilised world regards the name of Michael Faraday. No man was more fitted to discharge the duty we had imposed upon him than Fitzgerald; himself a man of singular originality, he possessed a fine critical insight and a power of just appraisement which, joined to a scrupulous love of truth and a contempt for the mere commonplaces of eulogy, made his estimate of the power and true place in science of Helmholtz one of the most weighty and most convincing contributions yet made to the series of our Memorial Lectures.

During the last Session of Parliament, the attention of the Council was directed to the possible influence of the Copyright Bill, then before a Committee of the House of Lords, upon the Society's activity as a publishing agency. The Bill, as originally drafted, appeared to affect our interests very considerably. Indeed, the position of journals like our own, which are largely concerned with scientific matter derived from foreign journals, to which our own Journal is equally accessible, had apparently not been considered by the promoters of the measure. Representations made to Lord Monkswell's committee, as the result of the consideration which was given to the subject by our Publication Committee, and by committees of societies

similarly affected, led to modifications in the Bill which largely, if not entirely, removed our objections. The measure, however, was not proceeded with in the Commons, and of course lapsed with the dissolution of Parliament. But it is to be reintroduced, I understand, during the present Session, and in its new form may need to be reconsidered by the Society.

As regards the Library, it appears that 810 books have been issued to Fellows during the last year, as against 790 during the previous year. The additions during the last year have been 102 books, 327 volumes of periodicals, and 30 pamphlets, as against 114 books, 397 volumes of periodicals, and 24 pamphlets in the previous year. Fifty-nine of the books have been presented by authors, publishers, and others.

A number of books and periodicals not bearing in any way on the work of the Society have been removed from the Library. Some proportion of these have been offered to, and accepted, by the British Museum, and the remainder will be disposed of either by presentation to kindred societies or by sale.

The books belonging to the Society are now distributed through various rooms in the building, not only in the Library proper, but also in the Tea Room, in the Council Room and in the Secretary's office. It is a matter of some anxiety to the Library Committee to make provision for the inevitable and necessary growth in the number of our books, and at the present rate of increase in our collection—and it is difficult to see how this can be greatly diminished—the time is not far distant when the whole of the available shelf-room will be occupied. From a careful measurement made for me by the Assistant Librarian, it appears that we at present possess 1786 feet of shelving, of which 1623 feet were occupied at the end of 1900. Some portion of this shelving already bears two rows of books, but it appears that little, if any, space can be gained by "backing," or by rearranging the position of the shelves in the cases. We have therefore not more than about 165 linear feet of shelf-space left in all the rooms together, and this, at our present rate of accumulation of books, will be wholly occupied within the next $2\frac{1}{2}$ years. The matter will no doubt soon require to be considered by the Library Committee. I am informed that the only other available storage place for books is the room adjoining the Meeting Room, hitherto known as the Preparation Room, and which to fit up as a library will need very considerable structural rearrangement.

On the last occasion I made reference to the fact that the condition of the Library Catalogue had received the attention of the Library Committee, and that on their recommendation the Council had decided that a new Catalogue should be prepared upon a plan

suggested by the Committee. It is now within sight of completion. The Author catalogue is finished, and consists of 4713 book entries and 1586 entries of pamphlets. The subject index is sufficiently advanced to allow of an estimate being made of its size; it will probably contain 5500 entries. The volume when printed will amount to about 360 pages. An estimate for printing is now in course of preparation.

The question of altering the day and hour of the Ordinary Meetings has recently been brought under the consideration of the Fellows. The expediency of making a change has been suggested on more than one occasion, and in fact the past records of the Society show that the Council have made alterations from time to time in the day of meeting on good cause shown, although, as might be anticipated, such changes have been invariably resisted by a minority. The Ordinary Meetings were originally on Tuesdays; the day was subsequently altered to Monday, and was changed to Thursday on the removal of the Society to its present quarters.

As the present day and hour have been so long in vogue, the Council resolved, rightly, in my opinion, to deprecate any change unless it could be shown to meet with the distinct approval of the greater number of the Fellows. It was urged by those who advocated the alteration that a great change had come over the social life of London during the sixty years of the Society's existence. A greater number of what used to be called the 'resident' Fellows now live in the suburbs which are extending in all directions, and are further and further removed from London proper. Moreover, it must not be lost sight of that the facilities for reaching town during recent years have so greatly increased that it seemed worth while to inquire whether a rearrangement of the day and hour of the meeting might not render it possible for the country Fellows to attend in greater numbers than hitherto. No better way of testing the question seemed to present itself than that of placing a definite suggestion before the general body of the Fellows, and of inviting them to express an opinion. A Committee, consisting of the officers and nominees of the Council and of the Fellows appointed to examine the replies which were received, reported that of the 1900 cards issued to Fellows, exactly 1000 were returned as replies. Of these 581 were unreservedly in favour of the change, namely, 256 London Fellows and 325 Country Fellows. 118 Fellows, whilst not voting unreservedly for the change, said they offered no objection to it. 172 Fellows were unreservedly opposed to the change. Of the 128 Fellows remaining, 88 expressed no objection to the change of day, but offered suggestions as to change of hour, 3 suggested meeting at 3, 1 at 4, 1 at 4.30, 12 at 5, 12 at 6, 9 at 6.30, 10 at 7, 5 at 7.30, 15 at 8, and 2 at 8.30. 11 suggested a later hour than 5.30 without particularising it, and 4

alternately 5.30 and 8. 24 Fellows suggested meeting on some other day than Wednesday or Thursday, namely, 2 on Monday at 5.30, 1 on Tuesday at 8, 14 on Friday, 10 of whom preferred 5.30. Of the remaining 4, 2 indicated no preference as to hour, 1 suggested 8, and 1 suggested 8.30. 7 Fellows suggested various hours on Saturday afternoon or evening. 16 Fellows preferred Thursday, but suggested some other hour than 8, 11 suggested 5.30, 1 preferred 6, and 3 preferred 7. 1 suggested 8.30. 4 Fellows deprecated the change on the ground that it clashed with the present arrangements of the Society of Public Analysts.

Analysing the voting cards of those Fellows who have contributed papers to the Society, 266 of whom have responded, 188 have voted for the change and 78 against it.

In view of this expresson of opinion, the Council came to the conclusion that it is desirable that the suggested change should be provisionally tried during the coming session. The Ordinary Meetings of next session will therefore be held on the 1st and 3rd Wednesdays of the month at 5.30. It is suggested that the Fellows should have the opportunity of meeting for tea about half an hour before the time at which the chair will be taken.

Experience can alone decide whether the alteration suits the general convenience of the Society.

For some time past our sister society in Berlin has had under consideration the desirability of establishing, with the co-operation of the various Chemical Societies in Europe and America, a uniform system of atomic weights. Professor Landolt, as chairman of the German Committee which initiated the suggestion, addressed an invitation to this Society to participate in the movement, and the Council appointed a small Committee to consider the question. On their report, it has been decided that we should take part in the formation of the International Committee suggested by the German Chemical Society, and that the delegates of this Society to the International Committee should be Professor Thorpe, Professor Tilden, Professor Dunstan, Dr. Scott, Professor Meldola, Sir William Crookes, Professor Dewar, and Dr. Russell. With a view of arriving, if possible, at a basis of agreement, or at least of narrowing the area of disagreement, the Committee, as desired, considered certain questions put before them by the German Chemical Society and it was decided to recommend

(1) That O = 16 be taken as the basis of calculation of atomic weights.

(2) That in assigning a number as the atomic weight of any element only so many figures should be employed that the last may be regarded as accurately known to one unit in that figure.

We have also concurred in the suggestion of the German Committee

that it would be desirable to form a small sub-committee of the international body of delegates to settle details when agreement has been reached upon points of principle, and we have nominated Dr. Scott as the British member of this Committee. These decisions have been communicated to the German Committee, and steps are being taken to form the International sub-Committee with a view to the compilation of the uniform table of atomic weights suggested.

In vacating the office to which, by your kindness, I was elected two years ago, it only remains for me to thank you for the consideration and forbearance which have been uniformly extended to me, not only during the term of my presidency, but also throughout the whole period of my official connection with the Society. This connection which, as a member of Council, as a Vice-President, as Treasurer, and, lastly, as President, has covered some 17 years, constitutes one of the happiest memories of my life. Those with whom I have worked have, I know, recognised with a generous appreciation that whatever may have been my shortcomings I have tried, to the best of my poor ability, to faithfully discharge the trust and obligation imposed upon me. And of this I am convinced, that whatever measure of success I may have had—whatever measure of approval I may have gained—is to be ascribed to the constant kindness and sympathetic co-operation of those with whom it has been my good fortune to be associated.

Dr. Armstrong proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed in the *Transactions*.

Prof. Smithells seconded the motion, which was carried by acclamation.

The President having returned thanks,

Prof. Tilden, F.R.S., the Treasurer, in giving an account of the Balance Sheet which he laid before the Society, duly audited, said :—

The receipts had been :—By admission fees and subscriptions, £4290 ; by sale of Journal and advertisements, £880 12*s.* 9*d.* ; and by dividends on invested capital, £464 14*s.* 4*d.* The total receipts from all sources amounted to £5668 19*s.* 8*d.* The expenses had been : —On account of the Journal, £3512 9*s.* 11*d.* ; on account of the Proceedings, £250 15*s.* ; on account of the preparation of a new Catalogue, £51 16*s.* 4*d.* ; on account of the Library, £238 15*s.* 11*d.* ; House expenses, £210 9*s.* 11*d.* ; the total expenditure being £4832 3*s.* 9*d.*

The Treasurer, in concluding, proposed a vote of thanks to the auditors, which was acknowledged by Mr. Page.

Prof. Emerson Reynolds, F.R.S., proposed a vote of thanks to the Officers and Council.

Prof. Collie, F.R.S., seconded the motion, which was unanimously adopted. Prof. Dunstan, F.R.S., responded.

The Scrutators having presented their report to the President, he declared that the following had been duly elected :—

President: J. Emerson Reynolds, D.Sc., M.D., F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, Bart., G.C.V.O., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Sir H. E. Roscoe, D.C.L., LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., Ph.D., D.Sc., LL.D., For.Sec.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: E. Divers, M.D., D.Sc., F.R.S.; C. E. Groves, F.R.S.; Prof. Herbert McLeod, F.R.S.; Prof. H. A. Miers, M.A., F.R.S.; T. Purdie, Ph.D., F.R.S.; T. Stevenson, M.D.

Secretaries: Wyndham R. Dunstan, M.A., F.R.S.; A. Scott, M.A., D.Sc., F.R.S.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: William A. Tilden, D.Sc., F.R.S.

Other Members of Council: H. Brereton Baker, M.A.; F. D. Chattaway, Ph.D., D.Sc.; Frank Clowes, D.Sc.; A. W. Crossley, Ph.D., D.Sc.; A. E. Dixon, M.D.; Prof. J. J. Dobbie, M.A., D.Sc.; H. J. H. Fenton, M.A., F.R.S.; M. O. Forster, Ph.D., D.Sc.; D. Howard; S. U. Pickering, M.A., F.R.S.; W. J. Pope; James Walker, D.Sc.

The Treasurer of the Chemical Society in Account with the Research Fund.

Dr. From March 24th, 1900, to March 23rd, 1901. Cr.

1900.		£	s.	d.	£	s.	d.
Mar. 24.	Balance at Bank, March 24, 1900				147	10	8
	Year's Dividends on £4,400 Metropolitan Board of Works 3½ per cent. Stock	146	18	10			
	Year's Dividends on £1,000 North British Railway 4 per cent. No. 1 Preference Stock	38	9	0			
	Year's Dividends on £1,034 Great Western Railway 2½ per cent. Debenture Stock	24	13	4			
					210	1	2
	Repayment of Unexpended Grants				11	2	5
	Repayment of Income Tax				4	1	0

1901.	*Assets.*	*Estimated Value.*					
Mar. 23.	Balance at Bank	192	15	3			
	£4,400 Metropolitan Board of Works 3½ per cent. Stock	4796	0	0			
	£1,000 North British Railway 4 per cent. No. 1 Preference Stock	1245	0	0			
	£1,034 Great Western Railway 2½ per cent. Debenture Stock	894	8	2			
		£7128	3	5			
					£372	15	3

1900.		£	s.	d.	£	s.	d.
June 20.	Grants to J. McCrae	5	0	0			
	,, F. C. Garrett	10	0	0			
	,, E. J. Russell	15	0	0			
	,, A. Lapworth	15	0	0			
	,, A. Lapworth	10	0	0			
					55	0	0
Dec. 20.	,, J. J. Sudborough	15	0	0			
	,, G. D. Lander	10	0	0			
	,, G. Young	10	0	0			
	,, W. J. Pope	50	0	0			
	,, J. Wade	10	0	0			
	,, H. O. Jones	10	0	0			
					105	0	0
	Longstaff Honorarium (Prof. Perkin, F.R.S.)				20	0	0
1901.							
Mar. 23.	Balance at Bank				192	15	3
					£372	15	3

Audited with vouchers and found correct. 23*rd March*, 1901.

Frederic Jas. M. Page.
E. W. Voelcker.
Alfred C. Chapman.

THE TREASURER IN ACCOUNT WITH THE CHEMICAL

Dr.

	£ s. d.	£ s. d.
Balance at Bank, March 24th, 1900	826 15 3	
,, in hands of Treasurer	0 2 8	
		826 17 11
Transferred from Deposit Account		500 0 0
Receipts by Life Compositions, Admission Fees and Subscriptions from March 24th, 1900, to March 23rd, 1901 :—		
Life Compositions—4 at £30, 2 Bal. at £28, 1 at £20, 2 at £15, 1 Bal. at £10, 3 at £12, 1 at £10	282 0 0	
116 Admission Fees	464 0 0	
1 Subscription for 1892 at £2	2 0 0	
1 ,, ,, 1893 ,, £2	2 0 0	
3 Subscriptions for 1894 ,, £2	6 0 0	
1 Subscription for 1896 at £2	2 0 0	
2 Subscriptions for 1897 ,, £2	4 0 0	
13 ,, ,, 1898 ,, £2	26 0 0	
99 ,, ,, 1899 ,, £2	198 0 0	
4 ,, ,, 1900 ,, £1	4 0 0	
677 ,, ,, ,, ,, £2	1354 0 0	
6 ,, ,, 1901 ,, £1	6 0 0	
970 ,, ,, ,, ,, £2	1940 0 0	
		4290 0 0
Sale of Journals	686 9 6	
,, Proceedings	12 16 0	
,, General Index : To the Public	14 4 0	
,, ,, ,, To Fellows	4 0 0	
,, Old Stock	15 10 0	
Proceeds of Advertisements in Journal	147 13 3	
		880 12 9
Subscription from the Society of Chemical Industry to June, 1900	8 8 0	
,, ,, ,, Public Analysts to January 1st, 1901	12 12 0	
,, ,, Physical Society to January 1st, 1901	12 12 0	
		33 12 0
Repayment of Income Tax	13 5 7	
Year's Dividends on £6,730 Metropolitan Board of Works 3½ per cent. Stock	224 15 3	
,, ,, £1,050 London and North-Western Railway Debenture Stock	30 1 1	
,, ,, £1,520 14*s.* 3*d.* Cardiff Corporation Stock	43 6 10	
,, ,, £1,400 India 2½ per cent. Stock	33 7 11	
,, ,, £2,358 Midland 2½ per cent. Preference	56 4 11	
,, ,, £2,400 Bristol 2½ per cent. Debenture	57 0 0	
Interest on Bank Deposit	6 13 4	
		464 14 11

Assets.	*Estimated Value.* £ s. d.
March 23rd, 1901.	
Balance at Bank (Current Account)	1313 12 7
,, ,, (on Deposit)	750 0 0
,, ,, in hands of Treasurer	1 3
£6,730 Metropolitan Board of Works 3½ per cent. Stock	7335 14 0
£1,050 London and North-Western Railway Debenture Stock	1097 5 0
£1,520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock	1475 1 7
£2,358 Midland Railway 2½ per cent. Preference	1921 15 4
£2,400 Bristol Corporation 2½ per cent. Debenture Stock	2052 0 0
£1,400 India 2½ per cent. Stock	1211 0 0
	£17,156 9 9

£6995 1[illegible] 7

SOCIETY, FROM MARCH 24TH, 1900, TO MARCH 23RD, 1901.

CR.

Expenses on Account of the Journal and Proceedings.

	£ s. d.	£ s. d.
Salary of Editor	250 0 0	
,, Sub-Editor	200 0 0	
,, Indexer	80 0 0	
Editorial Postages	14 6 10	
Abstractors' Fees	346 3 0	
Printing of Journal	1941 0 10	
Printing of Advertisements	23 13 2	
Printing Wrappers	97 10 0	
Distribution of Journal by Printers	357 11 6	
,, ,, Society	13 7 1	
Authors' Copies	85 14 0	
Illustrations for Journal	103 3 6	
		3512 9 11
Printing of Proceedings	178 13 8	
Distribution of Proceedings	72 1 4	
		250 15 0
Publishers' Commission	71 6 11	
Advertising Agents' Commission	22 2 10	
		93 9 9

Expenses on Account of the Library Catalogue.

Salaries	50 0 0	
Petty expenses	1 16 4	
		51 16 4

Expenses on Account of the Library.

Salary of Library Assistant	52 0 0	
Books and Periodicals	119 0 9	
Binding	67 15 2	
		238 15 11
Salary of Assistant Secretary		200 0 0
Pension to Mr. Hall		130 0 0
Miscellaneous Printing		87 19 3
Stationery		12 13 0
Address to the King		9 0 0
Indexing for International Catalogue		7 10 0
List of Fellows and Bye Laws		63 1 6

House Expenses.

Providing Refreshments	20 3 10	
Lighting the Building (Gas, £20 1*s.* 1*d.*; Electric Light, £25 10*s.* 6*d.*)	45 11 7	
Heating the Building (Coals)	21 8 9	
Cleaning	15 0 0	
Repairs	16 7 5	
Petty House Expenses	17 10 1	
House Porter's Wages	65 0 0	
,, ,, Uniform	7 0 0	
Annual Fee to Gate Porter	2 2 0	
Inhabited House Duty	0 6 3	
		210 9 11
Bank Charges, Treasurer's Stamps and Drafts		13 12 11
Treasurer's Petty Cash Disbursements		0 1 5
,, Assistant		10 0 0
Postage Account: Office and Secretarial Postages, £7 5*s.* 7*d.*; Postal Cards and Stamped Envelopes (Clay), £20 11*s.* 3*d.*; Embossed Stamps, £12 12*s.*		40 8 10
Transferred to Deposit Account		750 0 0
Balance at Bank		1313 12 7
,, in hands of Treasurer		0 1 3
		£6995 17 7

Audited with vouchers and found correct. } FREDERIC JAS. M. PAGE.
E. W. VOELCKER.
ALFRED C. CHAPMAN.

23*rd March*, 1901.

OBITUARY NOTICES.

Edmund Atkinson was born in 1831, at Lancaster, where his father carried on business as a pharmaceutical chemist. He was educated at the Lancaster Grammar School. After leaving school he entered his father's business, and at the same time became a student of the old Mechanics' Institute, in the working of which he took great interest, and in July, 1849, when only eighteen years of age, was elected a member of the committee of management. Shortly after this, he entered Owens College, then recently founded, where the late Sir Edward Frankland, the fir stProfessor of Chemistry, was among his tutors. After going through a course of study, he proceeded to Germany, spending three years at the Universities of Marburg, Heidelberg, and Göttingen, where he graduated as Ph.D., and then continued his studies under Adolphe Wurtz, in Paris. While working with Wurtz, he succeeded in considerably simplifying the preparation of acetate of glycol, a substance at that time of great interest, and "Atkinson's process" soon came into general use.

After returning to England, he spent some time at Queenwood College, Hampshire, where he was associated in the teaching staff with Tyndall, Hirst, and Debus. He then became assistant to the late Sir Benjamin Brodie, first in London and afterwards at Oxford. Subsequently he was appointed lecturer on chemistry and physics at Cheltenham College, and ranks as one of the earliest systematic teachers of these subjects in a large public school. From Cheltenham College, he passed on to the Royal Military College, Sandhurst, and afterwards to the Staff College, as Professor of Experimental Science.

In 1887 he retired from his Professorship, but continued to live near the Staff College, and for many years took an important and useful part in local affairs. One of the services that he rendered to his neighbours was that of obtaining the official recognition of the change of the name of the locality from Cambridgetown to the more euphonious Camberley.

He was elected a fellow of the Chemical Society in 1859, and was repeatedly a member of the Council. It was he who suggested that the Society's memorial to Faraday should take the form of a lectureship, to bear his name and to be held from time to time by a foreign man of science selected for the office by the Council.

He was one of the founders of the Physical Society, and was, with a short interval, treasurer of the Society from its foundation until a short time before his death.

Dr. Atkinson's services to science by the translation of numerous French and German works, among which we may specially mention

Ganot's "Physics," Helmholtz's "Popular Lectures," Dubois's "Magnetic Circuit," and Mascart and Joubert's "Electricity and Magnetism," are well-known. For many years, too, he contributed to the *Philosophical Magazine* periodical reports on chemical papers published in France and Germany. Of late years, however, these have been superseded by the much fuller and more systematic Abstracts published by the Chemical Society. He had an intimate knowledge of German, such as is not common among Englishmen, even when they are chemists, and was remarkably well read in English, French, and German literature. His clear-sighted, but genial, common sense caused his counsel to be much sought after by his many friends, and his kindly humour made his advice as pleasant to receive as it was profitable to follow.

Dr. Atkinson was married in 1869 to Mary Lang, daughter of Christopher Thomas, Esq., of Bristol. He died in May, 1900, after a very short illness, leaving four sons and two daughters.

Sir John Conroy, Bart., was born in 1845. He was the grandson of the first baronet, who was Equerry to the Duchess of Kent. He was educated at Eton and Christ Church, taking, in 1868, a first class in the Final Honour Schools of Natural Science. Leaving Oxford in that year, he devoted much of his time to original research. He published his first paper in our Journal in 1873. He returned in 1880 to Oxford as Science Tutor at Keble College. In 1887 he became Science Tutor at Balliol, being elected to a fellowship three years later. He was elected to the Royal Society in 1891. His original work comprises papers on the borderland of Physics and Chemistry. He published in all sixteen papers, "On the dioxides of calcium and strontium" (this Journal, 1873), "On the polarisation of light by crystals of iodine" (*Proc. Roy. Soc.*, 1876), "On the absorption spectrum of iodine" (*Proc. Roy. Soc.*, 1876), "On light reflected from potassium permanganate crystals" (*Phil. Mag.*, 1878), "On the distribution of heat in the visible spectrum" (*Phil. Mag.*, 1879), four papers on metallic reflection (*Proc. Roy. Soc.*, 1879, 1881, 1883, 1884), "Spectrum of the light emitted by a glow worm" (*Nature*, 1882), "A new photometer" (*Phil. Mag.*, 1883), "The amount of luminous and non-luminous radiation emitted by a gas flame" (*Proc. Roy. Soc.*, 1889), "The amount of light reflected and transmitted by certain kinds of glass" (*Phil. Trans.*, 1889), "The change in the absorption spectrum of cobalt glass produced by heat" (*Phil. Mag.*, 1891), "The refractive index of water at temperatures between 0° and 10°" (*Proc. Roy. Soc.*, 1895).

He was an ideal college tutor. His unfailing tact and real kindness

endeared him to all who knew him. Both his College and the University at large will feel his loss for many years to come. He died on December 15, 1900. By his will he left much valuable apparatus and a large sum of money for the benefit of the laboratory of the College which he had served so well. H. B. B.

By the death of Sir John Bennet Lawes, Bart., we have lost one who, for two generations, filled a conspicuous place in the world of chemistry and agriculture. He was born at the Manor House of Rothamsted, Herts, on December 28, 1814. His father, Mr. John Bennet Lawes, died when his son was eight years of age. The boy was sent to Eton, and afterwards to Brasenose College, Oxford, where he did not take a degree. He has described his youthful pursuits as "of a most desultory character"; they included the performance of chemical experiments at home, to the natural disgust of his elders. At the age of twenty he entered on the personal management of the family estate, which included a farm of 250 acres. One of his first acts was to fit up one of the rooms in the house as a laboratory. His chief chemical friend and instructor at this time was Dr. Anthony Todd Thomson, Professor of Materia Medica at University College. The inspiration thus afforded naturally led to pharmaceutical work. Medicinal plants were grown at Rothamsted, with the object of isolating their active principles. Dr. Thomson's process for making calomel and corrosive sublimate, by the combustion of mercury in chlorine gas, was started on a manufacturing scale in one of the barns belonging to the farm, but after some serious accidents was given up. The earliest experiments relating to agriculture began in 1837, plants being grown in pots with various manures. The pot experiments were continued in 1838 and 1839, and led to the discovery of the manurial value of superphosphates. The first phosphate treated with sulphuric acid was the waste animal charcoal of sugar works; apatite and other phosphates were soon treated in a similar way. In 1840 and 1841, the experience gained in pots was confirmed by trials on a larger scale in the field. In 1842, a patent was taken out for the manufacture of superphosphate.

The life work of Sir John Lawes divides itself at this point into two distinct branches. The manufacture and sale of superphosphate led him into a most successful career as a chemical manufacturer. The field experiments led, on the other hand, to the establishment and gradual development of the wonderful series of agricultural investigations now connected with the name of Rothamsted. We will glance first at his work as a chemical manufacturer.

The first chemical manure factory was established on Deptford Creek in 1843. The work soon outgrew the size of these premises, and, in 1857, 100 acres of land were purchased at Barking Creek, and a second and much larger factory erected. The whole of the manure business was sold in 1872 for £300,000.

Superphosphate was at first prepared from bones, bone-ash, waste animal charcoal, and apatite; the use of Suffolk (crag) coprolites and of Cambridge (green sand) coprolites followed. The vast deposits of mineral phosphates in other countries have since taken the place of English coprolites, and superphosphate is now chiefly prepared from South Carolinan, Floridan, Algerian, and Belgian phosphates. The total imports of phosphates to Great Britain in 1899 amounted to about 500,000 tons; this would probably yield about 900,000 tons of superphosphate. The manufacture abroad is on an equally large scale. The beneficial results which have followed the introduction of superphosphate as an agricultural manure are incalculable.

The manufacture of artificial manures was by no means the only enterprise in commercial chemistry conducted by Sir John Lawes. In 1866 he became, unwillingly, the owner of the tartaric and citric acid factory at Millwall, and at once proceeded to develop the work with his accustomed energy. He sent Mr. Grosjean to Sicily in 1868, and started the manufacture of citrate of calcium at Palermo, the citrate being sent to England in place of boiled lemon juice. He introduced the manufacture of tartaric acid from wine lees, in place of the crystallised tartar previously employed, and had agents abroad to purchase lees from the wine-makers. By these, and a variety of other economies and improvements, he was able, not only to withstand the powerful competition of Germany, but to increase the business till he became by far the largest producer of tartaric and citric acid in this country. Sir John Lawes was always ready to allow the publication of work done in his laboratories, and a number of papers by Warington and Grosjean, describing results obtained in the laboratory at Millwall, will be found in the Transactions of this Society, and in the *Journal of the Society of Chemical Industry*. Sir John Lawes had several other commercial ventures, including a large sugar estate in Queensland; but we need speak here only of work having a chemical interest.

We turn now to the agricultural investigations conducted at Rothamsted. While the commercial work was extending so rapidly in London, the agricultural researches were developing as quickly at home. In 1843 Sir John Lawes engaged Dr. (now Sir) J. H. Gilbert, who had previously acted as assistant to Dr. A. T. Thomson, to assist in the management of these researches. The association of Lawes and

Gilbert as agricultural investigators continued for fifty-seven years, and was only terminated by the death of Sir John Lawes.

Previously to the commencement of the Rothamsted investigations, the only systematic study of the problems of practical agriculture was that made by Boussingault, on his own farm at Bechelbronn: his researches were of great value, but were not permanently continued. The work at Rothamsted has been carried on continuously to the present day, and thus the Rothamsted station is now the oldest of the existing agricultural stations. The earliest German station, that at Möckern, dates from 1852; and the first American station, that at Middletown, from 1875. There are now several hundred stations in Europe and America. It is to the work done at these stations that we owe the gradual creation of agricultural science.

The development of the work at Rothamsted must now be noticed. In 1843 were commenced the systematic field experiments on turnips and wheat. The wheat field has grown wheat without intermission ever since. In 1847 the field experiments on beans commenced, and in 1848 those on clover, and on a four-course rotation. In 1851 the rotations of wheat and fallow, and wheat and beans were started. In 1852 the field experiments on barley commenced. In 1856 those on grass land. In 1869 those on oats. In 1870 those on sugar beet. In 1876 those on potatoes and mangel wurzel. In all, about forty acres were brought under experiment. The plan in every case was to grow the same crop year after year on the same land, both without manure, with farmyard manure, and with manures supplying nitrogen (as ammonium salts or nitrates), phosphates, and salts of potassium, sodium and magnesium in known quantities. The same kind of manure was applied every year to the same plot. The produce of each plot was carefully weighed, and at the laboratory the proportion of dry matter and ash was determined, while in selected instances the percentage of nitrogen was ascertained, and the plant ash was submitted to analysis. Later in the experiments the soil and subsoil of the plots have been subjected to chemical examination, and in the case of the wheat field the drainage waters from all the plots have also been analysed. Such, in few words, has been the scheme of the Rothamsted field experiments; the object in view has been to study the character of each crop, and to obtain statistics as to the influence of cropping and manuring upon the composition and fertility of the soil. Nowhere else have field experiments been attempted on such a comprehensive scale.

Experiments on sheep-feeding with various foods commenced in 1848. In 1848—1850, ten animals—oxen, sheep, and pigs—of various ages and condition as to fatness, were analysed; the water, fat, nitro-

genous matter and ash in the several parts of the body being determined. Subsequently the composition of the ash was ascertained. With the exception of the analyses of the bodies of pigs since made in America, these analyses still remain the only ones which have been attempted on farm animals. In 1850 an extensive series of pig-feeding experiments were made, which greatly helped to prove the production of fat from carbohydrates, and showed the fallacy of reckoning the nutritive value of foods from the proportion of nitrogenous constituents which they contained.

The old barn continued to be the only chemical laboratory at Rothamsted up to 1855. In 1854 a subscription was opened for a testimonial to Sir John Lawes, for his great services to agriculture; the testimonial at his request took the form of a laboratory, which was opened at a public gathering on July 19, 1855.* Large outbuildings have since been added for the storage of samples. In the new laboratory, the classical research on the assimilation of nitrogen by plants was carried out; the whole of the experimental work of this research was conducted by Dr. E. Pugh. Here, too, the numerous exact analyses of plant ash by Richter were made; and here in later years the researches on nitrification by Warington were conducted. The laboratory has also been largely used for the botanical analyses of the hay grown by various manures in the permanent grass experiments. In recent years, the determinations of nitrogen and nitric acid in the soils and subsoils of the experimental fields have occupied a large share of the laboratory work.

Investigations have also been conducted by outside workers on Rothamsted material, as the analyses of drainage waters by Voelcker and Frankland, and the recent laborious researches of Dyer on the amount and solubility of the phosphoric acid and potash in manured and unmanured soils of known history.

Among the important investigations conducted by Sir John Lawes we must not omit to mention his work on the Royal Commission appointed in 1857, "To inquire into the best mode of distributing the sewage of towns, and applying it to beneficial and profitable uses." Two members of this Commission, Lawes and Way, conducted for several years important experiments on sewage irrigation at Rugby: the investigation dealt with the quantity and composition of the grass manured with sewage, and its value as food for fattening oxen and milking cows, including the composition of the milk obtained. The effluent waters from the irrigated fields were also analysed, and the formation of nitrates in large quantities was demonstrated.

* Sir John Lawes' characteristic speech on this occasion has fortunately been preserved, see *Herts Guardian*, July 28, 1855, or *Gardeners' Chronicle and Agricultural Gazette*, July 15, 1871, p. 918.

Again, in 1863, the aid of Rothamsted was sought by the Government, the object in this case being to ascertain whether the malting of barley resulted in any increase of its value as a food. A considerable bulk of barley was divided into two lots, one of which was malted, and the loss in dry matter ascertained; feeding experiments were then made, in which the nutritive effect of a given weight of barley was compared with that shown by the quantity of malt which could have been produced from it. The trials with oxen, sheep, and pigs were made at Rothamsted, and those with milking cows at Rugby. The full report was presented to Parliament in 1866.

It is impossible to enumerate here the various reports on agricultural subjects which have issued from Rothamsted; these have appeared in very various publications, the majority of them in the *Journal of the Royal Agricultural Society*. Some of those communicated to the Chemical Society will be presently noticed. The collected Rothamsted reports now occupy ten volumes; copies of these have been presented by Sir John Lawes to numerous Institutions in this country and abroad. We should also mention the annual "Memoranda," giving an account of the manuring and produce of the experimental fields, and intended primarily as a guide to visitors. In middle life, Sir John Lawes was a frequent contributor of short practical papers to agricultural newspapers, both English and American. He also occasionally lectured to Farmers' Clubs and Agricultural Societies.

Sir John Lawes early formed the resolution of providing for the continuance of the work at Rothamsted after his own death. He made public mention of this intention at the opening of the new laboratory in 1855. When disposing of the manure business in 1872, he announced that he had set aside £100,000 as a permanent endowment of the Rothamsted Experiment Station. In 1889 the sum named was placed in the hands of trustees, and the future management of the institution was vested in a committee of nine members, nominated by the Royal Society, the Linnean Society, the Chemical Society, and the Royal Agricultural Society. As an example of private munificence for the furtherance of scientific investigation, the establishment, the maintenance, and the endowment of the Rothamsted Agricultural Experiment Station stands in this country without a parallel.

One provision of the trust deed should perhaps be noticed; it directs that a person shall be sent occasionally to the United States to lecture on the results of the Rothamsted experiments. Four courses of these lectures have been already given by R. Warington, J. H. Gilbert, H. E. Armstrong, and B. Dyer.

The jubilee of the Rothamsted experiments was celebrated on July 29th, 1893, the arrangements being made by the Royal Agricultural

Society. A meeting was held in front of the laboratory, the Minister for Agriculture (the Right Hon. Herbert Gardner) in the chair. Numerous addresses were presented to Sir John Lawes and to Dr. J. H. Gilbert by various public bodies, including one from the Chemical Society. Sir John Lawes also received his portrait painted by Herkomer, while Dr. Gilbert was presented with a piece of plate. A granite boulder with an inscription commemorating the fifty years of experimental work already accomplished was erected in front of the laboratory. Dr. Gilbert afterwards received the honour of knighthood from the Queen.

The honours bestowed on Sir John Lawes in recognition of his labours as an investigator were very numerous. He was elected a Fellow of the Royal Society in 1854, and in 1867 one of the Royal Medals was awarded to him and Dr. Gilbert. In 1882 Mr. Lawes was created a baronet. The degree of doctor was conferred on him by the Universities of Edinburgh, Oxford, and Cambridge. In 1894 the Albert Gold Medal of the Society of Arts was presented to Sir John Lawes and Sir Henry Gilbert "for their joint services to scientific agriculture, and notably for the researches which, throughout a period of fifty years, have been carried on by them at the Experimental Farm, Rothamsted." Foreign distinctions were equally numerous. He received a gold medal from the Imperial Agricultural Society of Russia. In 1881 the German Emperor awarded to Lawes and Gilbert a gold medal for agricultural merit. In 1893 Lawes and Gilbert received the Liebig Silver Medal from the Bavarian Academy of Sciences. Sir John Lawes was elected a corresponding member of the Institute of France in 1879, and was a Chevalier du Mérite Agricole, and a member of many Societies.

A few words must be said as to the relations between Sir John Lawes and the Chemical Society. He was elected a Fellow in 1850 and in 1862 became a member of the Council. His colleague, Dr. Gilbert, was a still earlier Fellow, and became a member of the Council in 1856. The work carried out at Rothamsted was chiefly concerned with the chemical aspects of agriculture, and was thus of the greatest interest to chemists. Feeling this, Sir John Lawes was in the habit of frequently inviting the members of the Council to Rothamsted during the month of June. In early days, when no railway had found its way to Harpenden, the chemists stayed at Rothamsted for the night, and after a day spent in studying the experiments in progress, devoted the evening to equally welcome relaxations, and, according to a well preserved tradition, sometimes played at leap-frog round the lawn! It was remarked at the commencement of this notice that the work at Rothamsted has already extended through the lives of two generations; this fact is brought vividly before one when

memory recalls the scenes of these early visits. The present writer can look back to chemical parties at Rothamsted, including Graham, Brodie, W. A. Miller, Mathiessen, Williamson, Hofmann, De la Rue, and Warington, senior.

The communications of Rothamsted work to the Chemical Society include four lectures by Dr. Gilbert—"The chemical statistics of the animal body," May 21, 1855; "The composition of the animal portion of our food, and on its relations to bread," Feb. 17, 1859; "The assimilation of nitrogen by plants," March 5, 1863; "The composition, value, and utilisation of town sewage," Feb. 1, 1866. Also a paper on the composition of wheat grain and its products in 1857; and a more complete investigation on the composition of the ash of wheat grain and wheat straw in 1884. The composition of soils was dealt with in a paper in 1885. There are also eighteen papers in the Transactions on work done in the Rothamsted laboratory by various investigators.

In conclusion, we must try to say a few words as to the man himself, the founder and inspirer of the work we have now described. It is almost needless to say that Sir John Lawes was a man of great physical vigour and untiring energy. When past 85 he still exhibited few of the infirmities of old age. He was a keen observer, and knew the experimental fields better than any of the Rothamsted workers. Not the fields only, but the birds and every living thing on the estate. The large amount of business he was able to get through was in no small degree due to his calm and cheerful temperament, which no disaster seemed to disturb. This quiet, self-contained temperament sometimes appeared as reserve or even shyness, and led to a reluctance to accept public positions or to take part in public functions; but his work doubtless gained by this refusal to expend his energy on outside occupations. The reserve we have mentioned was, however, a mood rather than a character, and disappeared the instant he was appealed to by any scientific or benevolent question. To speak to him of agricultural science would at once open the storehouse of thought and lead to a discourse of ready eloquence, interspersed with shrewd observations and humorous remarks.

Sir John Lawes was an enthusiastic investigator of agricultural problems, with the consideration of which his mind seemed to be continually occupied. His view of all questions was broad and statesmanlike, and he was cautious of adopting untried theories or recommending a new practice to farmers. Having farmed his own land all his life, he knew what was practicable for a farmer, and what were the necessary conditions of profitable work. With regard to his own achievements, no one could be more modest. He seemed without personal ambition. He rejoiced that the agricultural investigations

prospered, and looked forward to their growing in importance, but he was ever ready to ascribe their success to the workers whom he had gathered round him. Whatever may be the future of the Rothamsted experiments, the original mind cannot but be greatly missed. Teeming with suggestions and fresh views, carefully criticising results, grasping at once the practical bearing of each new fact, Sir John Lawes was throughout his life the inspirer and the best exponent of the Rothamsted experiments.

We speak in these pages of Sir John Lawes as a scientific man, but the record of his life would be very incomplete without some reference to his efforts to benefit the agricultural labourers of his parish and the workmen of his factories, and his readiness to help in every good work. Allotment gardens, co-operative stores, schools, mission rooms, and a savings bank were all started and continuously supported by him. One instance of his personal service shall suffice. Finding that the poor people of Harpenden did not like that others should know the extent of their savings, he used to come down himself on Saturday evening to receive their deposits. This savings bank was started by him in 1856, and continued till the opening of the Post Office banks.

Sir John Lawes died at Rothamsted after a short illness on August 31, 1900. R. W.

Stevenson Macadam was the second son of William Macadam, Burgess of Glasgow and delaine manufacturer in Kilmarnock, and was born in Glasgow in 1829. He received his first chemical instruction from his brother John at the Mechanics Institution in Glasgow, and afterwards proceeded to the University of Giessen, where he graduated as Doctor of Philosophy. On John leaving for Melbourne to take up the position of Professor of Chemistry in the newly started University there, Stevenson came to Edinburgh to occupy the position vacated by his brother of assistant to Dr. George Wilson. This post he held until Wilson became Professor of Technology in the University, when Macadam was appointed Extra-Mural Lecturer on Chemistry in the School of Medicine, Surgeons' Hall, which post he held until the time of his death.

Shortly after coming to Edinburgh, Stevenson Macadam was elected a Fellow of the Royal Society of Edinburgh and ever after took an active part in its work, contributing many papers as well as taking part in the general work of the Society. In 1856, he joined the Royal Scottish Society of Arts, to which he contributed in all some 44 papers and addresses, and was twice elected President.

In the formation of the Society of Chemical Industry he took a part and was one of the founders. Several papers were communicated by him to this Society and appear in the journal. He was also one of the founders of the Institute of Chemistry.

His published papers cover a wide range. In his earlier days he gave much attention to the physical side of chemistry, and his papers on such subjects are numerous and at the time received much attention. One of the first physical papers had as its subject the physico-chemical properties of gases, in which he referred especially to the specific gravity, solubility, diffusion, and transpiration, as well as dialysis and absorption, of this state of matter. This paper was printed in 1851. In the same year, a paper appeared in the *New Philosophical Journal* on "A new theory of the central heat of the earth and the cause of volcanic phenomena," as well as one on the "Cause of the phenomena exhibited by the geysers of Iceland." In 1852 and 1858, papers appeared in the same journal on the "General distribution of iodine," in which it was proved that that element did not occur in the atmosphere, in rain water, and in snow, as had been maintained by M. Chatin in a paper read before the Academy of Sciences, Paris. Water supply also took up much of Dr. Macadam's attention and led to the publication of many papers, not only on the subject of drinking waters and the sources of pollution, but also on the contamination of such by public works, &c.

The Tradeston flour mill explosion in 1872 led to an inquiry in which Dr. Macadam took an active part, and during the investigation of the cause it was shown, not only that flour might be highly explosive, but that this property was shared by coal dust, sawdust, and other finely divided substances.

In 1870, the Northern Lighthouse Board employed Dr. Macadam to investigate the illuminating properties of paraffin oil as well as the safety of such illuminant in lighthouses. This investigation proceeded until 1878, when, as the result of the work, all the Scotch lighthouses were illuminated by means of paraffin oil.

The valuation of fuels, both solid and liquid, received much attention and many investigations, and reports were published by him on this subject.

He conducted a large consulting practice, but yet found time for sport, and was a keen angler and otter hunter as well as a splendid walker and oarsman.

He died in January, leaving a widow, two sons (both Fellows of this Society), and two daughters.

XCIII.—*The Chlorine Derivatives of Pyridine. Part VII. Some Condensation Products.*

By W. J. Sell, M.A., F.R.S., and F. W. Dootson, M.A., D.Sc.

In Part III of this series of papers (Trans., 1899, 75, 979) a number of compounds were described as resulting from the action of dry chlorine on pyridine hydrochloride. Among these was a substance to which the empirical formula $C_{10}HN_2Cl_{11}$ was assigned, but no structural formula was offered. The present communication deals with some of the reactions of this compound, and the bearing which the results have on the constitution which should be assigned to it.

(1) In the communication referred to above, it was stated that the substance interacts with water, forming hydrogen chloride, and a new compound, also insoluble in water, having the molecular formula $C_{10}HON_2Cl_9$. In order, if possible, to gain a clearer insight into the relationship between the two compounds, a quantitative examination of the interaction was made. In the result, there remained no doubt that the reaction takes place according to the equation:

$$C_{10}HN_2Cl_{11} + H_2O = C_{10}HON_2Cl_9 + 2HCl.$$

With water at a higher temperature (120—130°), the substance darkens in colour, evidently decomposing, and in the liquid there is found 2-amino-3 : 4 : 5-trichloropyridine (Trans., 1900, 77, 771), held in solution by the hydrogen chloride also formed.

When the substance $C_{10}HN_2Cl_{11}$ is crystallised from ethyl alcohol, a similar interaction takes place, and the compound $C_{10}HON_2Cl_9$ is deposited.

The ready interaction with water and with ethyl alcohol, with the formation of an oxy-derivative, accompanied by hydrogen chloride in one case and alkyl chloride in the other, suggested the possibility that organic acids, for example, acetic or benzoic acid, might interact with formation of the acid chloride. This was found to be the case, a theoretical yield of benzoyl chloride being produced from benzoic acid. In the case of acetic acid, acetyl chloride was recognised as one of the products formed.

The crystalline residual product of these interactions was identical in properties and composition with that left by treatment of the parent substance $C_{10}HN_2Cl_{11}$ with water. Hence the change may be thus represented:

$$C_{10}HN_2Cl_{11} + C_6H_5{\cdot}CO_2H = C_{10}HON_2Cl_9 + C_6H_5{\cdot}COCl + HCl.$$

This behaviour is remarkable, and, so far as we are aware, is the first recorded instance in which the acid chloride has been formed by the interaction of an acid with a purely organic substance.

It may here be pointed out that, in the cases cited, the oxygen is in the OH condition. Ketonic oxygen does not appear to react under these conditions, inasmuch as the compound may be recrystallised unchanged from acetone.

(2) When the substance $C_{10}HON_2Cl_9$ is treated with a solution of sodium hydroxide and the resulting magma distilled in steam, a bulky crop of filamentous needles separates out from the distillate. This was found to be 2-amino-3 : 4 : 5-trichloropyridine (compare Part III, Trans., 1899, 75, 981 ; also Trans., 1900, 77, 771).

(3) Interesting results were obtained by treating the substance with sulphuric acid containing approximately 80 per cent. of the acid. The experiments were made under varying conditions of time and temperature. When the compound was merely dissolved in the acid at a temperature not exceeding 150°, and the whole poured into water as soon as solution had been effected, a white precipitate was obtained which on purification from acetic acid proved to have the composition $C_{10}HO_2N_2Cl_7$. The filtrate from this precipitate, on addition of ammonia in excess, yielded 2-amino-3 : 4 : 5-trichloropyridine.

It was, moreover, found that as the heating was continued for a greater length of time the yield of the substance $C_{10}HO_2N_2Cl_7$ diminished and that of the 2-amino-3 : 4 : 5-trichloropyridine increased until, in the maximum, a theoretical yield of the latter was obtained. When the substance, after being brought into solution, was rapidly raised to the boiling point and boiled, the products obtained were pentachloropyridine, hydrogen chloride, and carbon dioxide. At the same time, the liquid remained perfectly colourless, and contained 2-amino-3 : 4 : 5-trichloropyridine in solution.

(4) When the compound $C_{10}HN_2Cl_{11}$ is heated alone under diminished pressure, it melts, and at a higher temperature decomposes, yielding chlorine and pentachloropyridine. Nothing of a crystalline character has so far been recovered from the residue.

(5) A similar experiment was carried out with the substance $C_{10}HON_2Cl_9$, obtained from the parent compound by recrystallisation from acetic acid. In this case also, free chlorine was given off and pentachloropyridine distilled over. The experiment was stopped at an earlier stage than in the preceding one, and before complete decomposition had been effected. The residue, dissolved in acetic acid, on cooling yielded crystals melting at 225° and having the composition $C_{10}HON_2Cl_7$.

(6) The same substance, $C_{10}HON_2Cl_7$, was also obtained by reduction of the compound $C_{10}HN_2Cl_{11}$ by means of anhydrous stannous

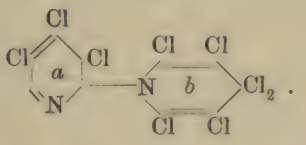
chloride in acetone solution, and subsequent recrystallisation of the reduced product from acetic acid.

From these facts, the following appear to be legitimate deductions.

I. That the compound $C_{10}HN_2Cl_{11}$ consists of two pyridine nuclei linked by the 2-position of the one (which for reference may be called the *a* ring) to the nitrogen atom of the other (*b* ring) (compare 2 and 3, above).

II. That the hydrogen atom of the compound $C_{10}HN_2Cl_{11}$ occupies the 6-position in the *a* ring.

III. That the *b* ring, since it is capable of yielding pentachloropyridine, must contain at least six chlorine atoms, as shown by the formula,

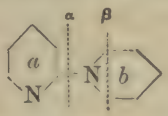


The two additional atoms of chlorine contained in the molecule which are still unaccounted for in this formula are regarded as being united to the *b* ring for the following reasons.

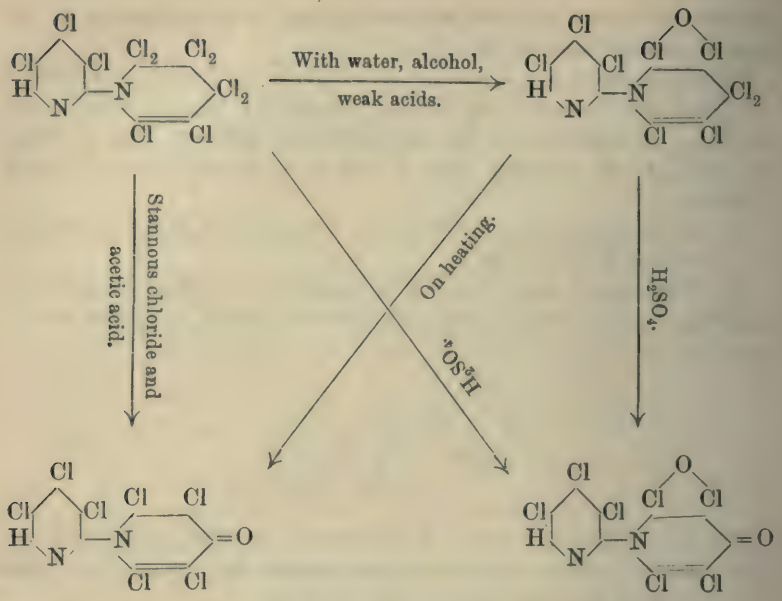
1. The oxy-derivative of the formula $C_{10}HON_2Cl_9$ yields, on heating either pentachloropyridine, or a compound, $C_{10}HON_2Cl_7$, according to the conditions of the experiment. The latter, with sulphuric acid, yields 2-amino-3 : 4 : 5-trichloropyridine, but cannot be made to yield pentachloropyridine by any of the reactions mentioned above.

2. The compound $C_{10}HO_2N_2Cl_7$, obtained by the action of sulphuric acid on the parent substance $C_{10}HN_2Cl_{11}$, may be made to yield 2-amino-3 : 4 : 5-trichloropyridine, but no pentachloropyridine.

It may be observed that when decomposition takes place it has only hitherto been possible, in the same change, to isolate derivatives from *one* ring which throw any light on the constitution of the compounds, (the cleavage of the molecule following the line α or β),



as is shown in the quantitative experiments described later. The chief derivative of the *a* ring is 2-amino-3 : 4 : 5-trichloropyridine; of the *b* ring, pentachloropyridine. It is possible, and even probable, that there are tautomeric forms of the compound. With this reservation, the changes and formulæ described above may be represented in the following way (p. 902):



Experimental.

Interaction with Water.—A quantity of the substance, $C_{10}HN_2Cl_{11}$, weighing 0·7925 gram was heated on the water-bath with 50 c.c. of water for 3 hours and then filtered. The filtrate, after neutralisation with pure chalk, was found to require 29 c.c. of *N*/10 silver nitrate for complete precipitation. This indicates that, by interaction with water, 100 grams of the compound give 13·35 grams of hydrogen chloride. The equation

$$C_{10}HN_2Cl_{11} + H_2O = C_{10}HON_2Cl_9 + 2HCl$$

requires the production of 13·53 grams of hydrogen chloride from 100 grams of the compound.

Interaction with Alcohol.—The parent substance, $C_{10}HN_2Cl_{11}$, dissolved in boiling alcohol, on cooling deposited crystals melting at 171—172° (uncorr.) which were analysed with the following results:

0·5790 gave 0·5250 CO_2 and 0·0127 H_2O. C = 24·73; H = 0·24.
0·2200 ,, 0·5870 AgCl. Cl = 65·99.
$C_{10}HON_2Cl_9$ requires C = 24·82; H = 0·21; Cl = 65·86 per cent.

Interaction with Benzoic and Acetic Acids.—In the case of benzoic acid 2 grams of the acid were mixed with 10 grams, or rather more than the theoretical quantity, of the chlorinated derivative, and the mixture distilled from a metal-bath. The distillate, which weighed 2·3 grams,

was almost pure benzoyl chloride, as shown by its boiling point and general properties, and was gradually resolved by interaction with water into a solid mass of crystals of benzoic acid. The residue left in the distillation flask was recrystallised from acetic acid and was found, by its melting point and general character, to be identical with the product formed by interaction of the substance $C_{10}HN_2Cl_{11}$ with water or alcohol. The equation

$$C_{10}HN_2Cl_{11} + C_6H_5{\cdot}CO_2H = C_6H_5{\cdot}COCl + C_{10}HON_2Cl_9 + HCl$$

requires that 2 grams of benzoic acid should produce 2·3 grams of benzoyl chloride, so that the yield obtained is seen to be quantitative.

When acetic acid was substituted for benzoic acid in the above experiment, a distillate was obtained from which acetyl chloride was isolated by fractionation.

Interaction with Sodium Hydroxide.—Since the parent substance $C_{10}HN_2Cl_{11}$ invariably yields the monoxy-derivative, $C_{10}HON_2Cl_9$, on treatment with water as shown above, the latter substance was used in this experiment. Ten grams of this material were treated with an excess of dilute sodium hydroxide (1 in 10) and distilled with steam until nothing further was carried over. The aqueous distillate on cooling deposited the calculated quantity of 2-amino-3 : 4 : 5-trichloro pyridine, recognised by its melting point (159—160° uncorr.), and a nitrogen determination.

0·3827 gave 46·7 c.c. nitrogen at 19° and 764 mm. N = 14·11.

$C_5H_3N_2Cl_3$ requires N = 14·20 per cent.

So far, nothing crystalline has been isolated from the contents of the distillation flask.

Interaction with Sulphuric Acid containing 80 *per cent. of* H_2SO_4.—The first product of the interaction of sulphuric acid on the parent substance under the conditions tried is the compound $C_{10}HON_2Cl_9$ in all cases. Ten grams of the latter were heated to incipient boiling with 100 c.c. of acid, but not boiled. Hydrogen chloride was freely evolved, and on cooling the mass was poured into several times its volume of water. The precipitate was collected, washed, and dried, and was found to weigh 1·6 grams. On recrystallisation from glacial acetic acid, this compound was obtained in large, lustrous cubes which melted at 146—147° (uncorr.), and furnished the following numbers on analysis :

0·3149 gave 0·3195 CO_2 and 0·0067 H_2O. C = 27·73 ; H = 0·23.

0·2905 ,, 17·4 c.c. nitrogen at 17° and 759 mm. N = 6·95.

0·1546 ,, 0·3603 AgCl. Cl = 57·66.

$C_{10}HO_2N_2Cl_7$ requires C = 27·90 ; H = 0·23 ; N = 6·51 ; Cl = 57·85 per cent.

The filtrate from the above, on being made alkaline with ammonia,

deposited a bulky crop of filamentous needles, weighing 3·2 grams after washing and drying. These, on recrystallisation and subsequent analysis, proved to be 2-amino-3 : 4 : 5-trichloropyridine, melting at 159—160° (uncorr.). A nitrogen determination was made, with the following result :

0·2192 gave 27·5 c.c. nitrogen at 22° and 762 mm. N = 14·25.
$C_5H_3N_2Cl_3$ requires N = 14·20 per cent.

On calculating the weight of the precipitate above into the corresponding weight of the material which was originally taken (1·6 grams corresponds to 1·8 grams), and subtracting this from the 10 grams used, it will be seen that 8·2 grams of the compound $C_{10}HON_2Cl_9$ underwent the more complete decomposition. This amount should yield theoretically 3·3 grams of aminotrichloropyridine, as against 3·2 grams actually found.

In a second experiment, 10 grams of the compound were heated with 170 c.c. of 80 per cent. sulphuric acid in a distillation flask immersed in a metal-bath, the temperature being gradually raised to 160° and maintained there for 45 minutes. On cooling, the contents of the flask were distilled with steam until practically nothing further was carried over. From the aqueous distillate, 1·3 grams of pentachloropyridine were obtained by filtration. The contents of the distilling flask deposited nothing on standing for 24 hours, but on addition of ammonia yielded a crop of crystals of 2-amino-3 : 4 : 5-trichloropyridine, which, after washing and drying, weighed 2·8 grams. The latter weight is the theoretical yield of aminotrichloropyridine from 6·8 grams of the substance $C_{10}HON_2Cl_9$ taken. The material not thus accounted for, 3·2 grams, should theoretically yield 1·6 grams of pentachloropyridine, as against 1·3 grams actually obtained.

A further experiment, in which the interaction of sulphuric acid with the compound $C_{10}HON_2Cl_7$ was studied, showed by its yielding 2-amino-3 : 4 : 5-trichloropyridine that the former is essentially a derivative of the parent substance $C_{10}HN_2Cl_{11}$, from which it has been obtained by reduction with stannous chloride and subsequent recrystallisation from acetic acid, as also by partial decomposition by heat of the hydrolysed product, $C_{10}HON_2Cl_9$.

Influence of Heat.—The parent substance, $C_{10}HN_2Cl_{11}$, was heated in a distillation flask with a wide delivery tube immersed in a metal-bath and under a pressure of 15—20 mm. Beyond melting, no change was observed to take place until the temperature of the bath reached 230—240°, when an oil distilled over which solidified in the delivery tube. As the temperature of the bath approached 260°, the amount of the distillate increased, and the apparatus was full of chlorine. On every occasion at this stage a slight explosion was noticed, which was

succeeded by an increased flow of liquid in the delivery tube. The temperature of the bath was slowly raised to 300°, when the experiment was stopped.

The residue, which was light brown in colour and showed no traces of charring, was completely soluble in glacial acetic acid, imparting to it an intense greenish-yellow fluorescence, but nothing crystalline could be obtained from it. The distillate gave a very pure specimen of pentachloropyridine, identified by its melting point (124—125° uncorr.) and by a chlorine determination.

0·1296 gave 0·3700 AgCl. Cl = 70·66.

C_5NCl_5 requires Cl = 70·51 per cent.

A repetition of the above experiment in which the temperature of the bath was not allowed to exceed 270° led to precisely similar results.

In view of the foregoing, it became of interest to examine the effect of heat on the oxy-derivative of the original substance. With this object, 20 grams of the compound $C_{10}HON_2Cl_9$ were heated in a similar way, the condenser in this case containing crystals of potassium iodide moistened with water. The volatile products were the same, namely, chlorine (which, of course, reacted in part with the potassium iodide) and pentachloropyridine. The reaction was in this case stopped when the temperature of the bath reached 270° and the pentachloropyridine was still coming over. The residue was recrystallised from acetic acid, and the first crop of crystals, melting at 225—226° (uncorr.), was analysed, with the following results:

0·5815 gave 0·6317 CO_2 and 0·0111 H_2O. C = 29·62; H = 0·21.

0·3405 „ 0·8246 AgCl. Cl = 59·82.

$C_{10}HON_2Cl_7$ requires C = 29·07; H = 0·25; Cl = 60·00 per cent.

It is thus seen that the compound $C_{10}HON_2Cl_7$, obtained by incomplete chlorination of pyridine hydrochloride (Trans., 1899, 75, 980) and by the reduction of the parent substance, $C_{10}HN_2Cl_{11}$, by stannous chloride and subsequent crystallisation from acetic acid, may also be obtained by heating the oxy-derivative, $C_{10}HON_2Cl_9$.

Reduction by means of Stannous Chloride.—The compound $C_{10}HN_2Cl_{11}$ was dissolved in acetone containing an equal weight of anhydrous stannous chloride. The mixture, when heated on the water-bath in a reflux apparatus, reacted energetically. The product obtained on dilution was recrystallised from acetic acid, from which it separated in rectangular prisms melting at 223—224° (uncorr.). A chlorine determination furnished the following numbers:

0·2098 gave 0·5050 AgCl. Cl = 59·75.

$C_{10}HON_2Cl_7$ requires Cl = 60·00 per cent.

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XCIV.—*The Action of Lead Thiocyanate on the Chlorocarbonates. Part II. Carboxymethyl- and Carboxyamyl-thiocarbimides and their Derivatives.*

By Robert Elliott Doran.

In the Society's Transactions for 1896 (p. 324, *et seq.*), the author described the preparation and properties of carboxyethylthiocarbimide, and dealt with the further proof which it afforded of the generic character of the interaction, discovered by Miquel, which occurs when certain of the acidic chlorides are heated under suitable conditions with lead thiocyanate. The present communication is chiefly concerned with the homologous methyl compound, and as the methods of preparation were usually carried out in the same way as those described in Part I., briefer details will be sufficient.

Preliminary experiments showed that there was no apparent sign of interaction when methyl chlorocarbonate alone was heated with lead thiocyanate, and only traces of a thiocarbimide could be detected when the mixture was diluted with benzene and again heated. When, however, a mixture of benzene and toluene was used as solvent for the chlorocarbonate, interaction took place fairly readily on heating, and was completed, as a rule, after ten to twenty minutes' boiling. Working on a larger scale, 20 grams of methyl chlorocarbonate were dissolved in a mixture of equal volumes of benzene and toluene, and added, in a flask, to a quantity of dry lead thiocyanate about one and a-half times that required by the equation:

$$2CH_3O\cdot COCl + Pb(SCN)_2 = 2CH_3O\cdot CO\cdot NCS + PbCl_2.$$

The flask was connected with a reflux apparatus, and the mixture, with frequent shaking, cautiously heated to boiling. Interaction set in rapidly, as was indicated by a change of colour in the liquid and in the lead salt, but brisk ebullition had to be maintained for upwards of twenty minutes before the liquid (now bright yellow), when cooled and allowed to clear by subsidence, was found to be free from chlorine. The lead chloride and unchanged thiocyanate were removed by filtration, washed with benzene, and the filtrate further diluted with this solvent until, assuming an approximately quantitative yield, each c.c. should contain 0·5 gram of the thiocarbimide. From this solution, some of the derivatives to be described presently were prepared. It is desirable to note here that the yields of the thiocarbimide, as estimated from the yields of its derivatives, only approached that theoretically obtainable on one or two occasions. Much greater difficulty has, in fact, been experienced in getting complete interaction

between methyl chlorocarbonate and lead thiocyanate than between its ethyl homologue and the same salt. So far, the cause of this has not been ascertained, but it has been noticed occasionally that the formation of the thiocarbimide apparently stopped when rather less than half the chlorocarbonate taken had undergone change. No variation in the amount of solvent used, or in the relative proportions of its constituents, or the use of toluene alone, with the object of getting a higher temperature, appeared to have any appreciable effect in completing the interaction; whilst the possible influence of mass and of surface coating of the thiocyanate was eliminated as far as possible, both by the use of a very large excess of the lead salt and by filtering off that partly acted on, replacing it by a fresh charge and reheating. An extended series of experiments was made with several of the other thiocyanates, those of silver, mercury, ammonium, and potassium being tried, and the last-named was the only one that gave anything like satisfactory results. It has been found that when methyl, ethyl, or amyl chlorocarbonate is diluted with dry benzene and allowed to stand in contact with dry, finely-powdered potassium thiocyanate, interaction commences at the ordinary temperature on the third or fourth day (when the clear liquid becomes faintly yellow and gives a slight but distinct black precipitate with ammoniacal silver nitrate), and continues until, after a period of two to three months, it *approaches* completion. Unfortunately, however, whilst there is still unchanged chlorocarbonate present, decomposition sets in, accompanied by the formation of mercaptans, chlorides, carbon dioxide, and an amorphous, orange-yellow solid, insoluble in water, which has not yet been examined; nevertheless the greater part of the chlorocarbonate used undergoes change in accordance with the equation:

$$R'O\cdot COCl + KSCN = R'O\cdot CO\cdot NCS + KCl.$$

Solutions of carboxymethylthiocarbimide obtained in this way have been used in the preparation of some of the derivatives to be described later. The action of heat appears to have little effect in increasing the rate at which the change takes place, unless the operation is conducted under pressure, when, in two experiments made at the temperature of the water-bath, it resulted in decomposition with explosive violence.

On account of the poor yields, and partly on account of the fairly complete examination of the corresponding ethyl compound (*loc. cit.*), no attempt was made to isolate carboxymethylthiocarbimide. Its properties, as determined in solution, in respect to its action on desulphurising agents, and lack of any action on ferric chloride, are identical in every way with those of its homologue, EtO·CO·NCS. It

was found that the presence of upwards of 50 per cent. of unchanged chlorocarbonate did not affect the preparation of the derivatives described, although of course it resulted in the simultaneous formation of the urethanes and hydrochlorides corresponding to the individual amines used, as well as the required sulphuretted compound, in accordance with the general equation,

$$MeO{\cdot}COCl + 2R'{\cdot}NH_2 = MeO{\cdot}CO{\cdot}NHR' + R'{\cdot}NH_2{,}HCl.$$

As the hydrochlorides thus formed are practically insoluble, and the urethanes usually freely soluble in benzene, whilst the thiocarbamides and thioureas as a rule occupy a conveniently intermediate position, the separation and purification of the last, when obtained in sufficient quantity, were readily effected.

Turning now to the derivatives themselves, it will prevent unnecessary repetition to state beforehand that they were all prepared in the same way, by adding the bases, dissolved in benzene or alcohol, to the benzene or benzene-toluene solution of the thiocarbimide, in the proportions required by the equation,

$$R'{\cdot}NH_2 + MeO{\cdot}CO{\cdot}NCS = MeO{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}R'.$$

Interaction occurred immediately with development of heat, and usually with separation of a solid consisting of the required thiocarbamide or thiourea, or mixtures of them with the hydrochloride of the base used, in those cases where the parent substance was not obtained free from unchanged chlorocarbonate. In all instances where no definite yield is mentioned, this condition prevailed in a greater or less degree.

Aromatic Derivatives.

ab-*Carboxymethylphenylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5$. —This substance was obtained from aniline and the thiocarbimide. When recrystallised from alcohol, it formed long, white needles melting at 158° without decomposition. On analysis:

0·2008 gave 0·2248 $BaSO_4$. S = 15·39.

$C_9H_{10}O_2N_2S$ requires S = 15·25 per cent.

The compound is freely soluble in hot, but only sparingly so in cold, alcohol or benzene, and is sparingly soluble in hot water. In alcoholic solution, it is readily desulphurised on warming with neutral silver nitrate, or on boiling with alkaline lead tartrate, and at once in the cold with alkaline silver nitrate.

ab-*Carboxymethylbenzylthiocarbamide*,

$$CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5.$$

—Only a very poor yield of this derivative was obtained, and when

recrystallised from aqueous alcohol, from which it separated in tufts of needles, it melted at 134° without decomposition.

0·124 gave 0·130 $BaSO_4$. S = 14·41.

$C_{10}H_{12}O_2N_2S$ requires S = 14·3 per cent.

It is freely soluble in hot, and moderately so in cold, alcohol or benzene, but is insoluble in water. Its alcoholic solution gives a white precipitate, blackening on heating, with neutral silver nitrate, an immediate black precipitate with the ammoniacal nitrate, and is slowly desulphurised on boiling with alkaline lead solution.

ab-*Carboxymethyl-o-tolylthiocarbamide*,

$CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$.

—The yield of the crude product amounted to 96 per cent. of the theoretical. The pure substance melted at 172° without decomposition.

0·1999 gave 0·2092 $BaSO_4$. S = 14·38.

$C_{10}H_{12}O_2N_2S$ requires S = 14·30 per cent.

The compound is moderately soluble in hot, and sparingly so in cold, benzene or alcohol, separating from the former in needles and from the latter in feathery plates. It is insoluble in water. With desulphurising agents, it behaves like the phenyl derivative.

ab-*Carboxymethyl-p-tolylthiocarbamide*,

$CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$.

—A 35 per cent. yield was obtained in the form of thick, short prisms melting at 158° without decomposition.

0·20 gave 0·2101 $BaSO_4$. S = 14·44.

$C_{10}H_{12}O_2N_2S$ requires S = 14·30 per cent.

For all practical purposes, the properties of this compound are identical with those of the *o*-derivative.

ab-*Carboxymethyl-α-naphthylthiocarbamide*,

$CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7$.

—This compound crystallises from alcohol in tufts of long, flexible needles melting at 193° with copious effervescence.

0·2212 gave 0·20 $BaSO_4$. S = 12·43.

$C_{18}H_{12}O_2N_2S$ requires S = 12·32 per cent.

The substance is moderately soluble in hot, and sparingly so in cold, benzene, rather sparingly soluble in hot, and nearly insoluble in cold, alcohol, and is insoluble in water. The behaviour of this and the following compound, with the usual reagents for the removal of sulphur, is practically the same as that of the tolyl derivatives.

ab-*Carboxymethyl-β-naphthylthiocarbamide*,

$CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_{10}H_7$.

—By recrystallisation from mixed alcohol and benzene, this compound

was obtained in microscopic needles melting at 184° with decomposition.

0·2014 gave 0·1822 $BaSO_4$. S = 12·43 per cent.

It is freely soluble in hot, and moderately so in cold, benzene, sparingly soluble in hot, and nearly insoluble in cold, alcohol, and very sparingly soluble in hot water.

Fatty Derivatives.

ab-*Carboxymethylmethylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}CH_3$.—This compound was obtained in the form of fine, white needles melting at 146° without decomposition.

0·2028 gave 0·3219 $BaSO_4$. S = 21·8.

$C_4H_8O_2N_2S$ requires S = 21·63 per cent.

It is moderately soluble in hot, and sparingly so in cold, alcohol, benzene, or water. Its alcoholic solution gives a white precipitate with neutral silver nitrate, which blackens on heating; it is at once desulphurised by the ammoniacal nitrate, but only darkens slightly on prolonged boiling with alkaline lead solution.

ab-*Carboxymethylethylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_2H_5$, occurs in tufts of white, feathery needles melting at 86° without decomposition.

0·203 gave 0·295 $BaSO_4$. S = 19·9.

$C_5H_{10}O_2N_2S$ requires S = 19·76 per cent.

The compound is freely soluble in hot or cold alcohol or benzene, moderately so in hot, but sparingly so in cold, water, and is nearly insoluble in cold light petroleum. With desulphurising agents, it reacts like the preceding compound.

ab-*Carboxymethylisobutylthiocarbamide*, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_4H_9$.—This substance, of which only a very poor yield was obtained, crystallises from light petroleum in long prisms melting at 83° without decomposition.

0·153 gave 0·1895 $BaSO_4$. S = 17·02.

$C_7H_{14}O_2N_2S$ requires S = 16·85 per cent.

It is freely soluble in hot or cold alcohol or benzene, moderately so in hot, and only sparingly so in cold, light petroleum. It behaves like the methyl and ethyl derivatives with lead and silver salts.

Carboxymethylthiourea, $CH_3O{\cdot}CO{\cdot}N{:}C(NH_2){\cdot}SH$.—On passing a stream of ammonia through a quantity of the benzene-toluene solution of the thiocarbimide, vigorous action occurred, accompanied by the evolution of heat and traces of hydrogen sulphide. A little solid

separated while the liquid was still hot, and on cooling a considerable crop of crystals was obtained which, when collected, washed with benzene and recrystallised, first from water and then from alcohol, from which it separated in short prisms, melted at 166° with copious effervescence, the gas evolved being apparently methyl mercaptan.

0·20 gave 0·348 $BaSO_4$. S = 23·92.

$C_3H_6O_2N_2S$ requires S = 23·89 per cent.

The substance is moderately soluble in hot, sparingly so in cold, benzene, freely but slowly soluble in hot, and sparingly so in cold, alcohol, moderately so in hot, and nearly insoluble in cold, water. Its aqueous solution is readily desulphurised by the usual reagents, and gives a very fine mirror of lead sulphide with alkaline lead tartrate.

Trisubstituted Thioureas.

Of these, three were prepared, from piperidine, and methyl- and benzyl-anilines, but only one of them, that derived from the first-named base, was obtained in quantity sufficient for satisfactory identification.

Carboxymethylpiperidylthiourea, $CH_3O\cdot CO\cdot N{:}C(SH)\cdot NC_5H_{10}$. — The yield of the crude substance amounted to 11 per cent. of the theoretical. When purified by recrystallisation, firstly from mixed benzene and light petroleum, secondly from the latter solvent alone, and thirdly from water, it melted at 97°.

0·205 gave 0·2355 $BaSO_4$. S = 15·8.

$C_8H_{14}O_2N_2S$ requires S = 15·77 per cent.

It is very freely soluble in benzene, alcohol, ether, chloroform, or acetone; but only sparingly so in hot, and nearly insoluble in cold, water or light petroleum. Its alcoholic solution is not visibly affected by prolonged boiling with alkaline lead solution, and only darkens slightly under the same conditions with ammoniacal silver nitrate.

Carboxymethylphenylsemithiocarbazide,

$$CH_3O\cdot CO\cdot NH\cdot C(SH){:}N\cdot NH\cdot C_6H_5.$$

—Vigorous action occurred when phenylhydrazine, dissolved in alcohol, was added to a benzene-toluene solution of carboxymethylthiocarbimide. A solid separated almost at once, and by recrystallisation from alcohol was eventually obtained pure in the form of white, glistening plates melting at 180°, and remelting at the same temperature.

0·2078 gave 0·215 $BaSO_4$. S = 14·22

$C_9H_{11}O_2N_3S$ requires S = 14·23 per cent.

The substance is moderately freely but slowly soluble in hot, and

is nearly insoluble in cold, alcohol, sparingly so in hot benzene, and insoluble in water. Its alcoholic solution, with neutral silver nitrate, gives a white silver salt which blackens slowly on heating, and shows the usual reactions characteristic of a hydrazine derivative with copper sulphate and ferric chloride.

Thiocarbamates.

Three of these were prepared by mixing an excess of the corresponding alcohols with a benzene solution of the thiocarbimide. They were obtained by allowing the benzene and excess of alcohol to evaporate spontaneously, and were purified by recrystallisation from light petroleum in the case of the first two, and from aqueous alcohol in the case of the benzyl compound. In alcoholic solution, they all gave white silver salts, which blackened at once on heating, after the addition of ammonia.

Methyl Carboxymethylthiocarbamate, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}O{\cdot}CH_3$.—White, feathery needles melting at 46°.

0·2042 gave 0·3198 $BaSO_4$. S = 21·53.

$C_4H_7O_3NS$ requires S = 21·49 per cent.

Ethyl Carboxymethylthiocarbamate, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}O{\cdot}C_2H_5$.—Long needles melting at 83°.

0·205 gave 0·296 $BaSO_4$. S = 19·85.

$C_5H_9O_3NS$ requires S = 19·65 per cent.

Benzyl Carboxymethylthiocarbamate, $CH_3O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}O{\cdot}CH_2{\cdot}C_6H_5$.—Tufts of fine, creamy-white needles melting at 103°.

0·2084 gave 0·220 $BaSO_4$. S = 14·51.

$C_{10}H_{11}O_3NS$ requires 14·24 per cent.

In Part I of this communication, to which reference has already been made, it was shown, when dealing with the "constitution of nitrogen bases and isomerism," that Seidel's so-called "ethyl *iso*phenylthioallophanate" (*J. pr. Chem.*, 1885, [ii], **32**, 261) was identical with the author's *s*-carboxyethylphenylthiocarbamide, and that Seidel's statement that the group RO·CO· was "negative" to R′CO, and could be expelled by it from compounds of the type specified, was incorrect. In fact, the very opposite was established in the case then under investigation, since it was found that carboxyethylphenylthiocarbamide remained unchanged after heating with a large excess of acetyl chloride, whilst the converse change was readily effected by heating acetylphenylthiocarbamide with ethyl chlorocarbonate,

$$CS\langle^{NHPh}_{NHAc} + EtO{\cdot}COCl = CS\langle^{NHPh}_{NHCO{\cdot}OEt} + AcCl,$$

the product being in every respect identical with that obtained by the direct union of aniline with carboxyethylthiocarbimide. Since this result was published, the author has prepared several other carboxyethyl derivatives by heating various acetylthioureas with EtO·COCl, and, in the course of the present investigation, has further established the *positive* character of the group R′O·CO, so far as the group CH_3·CO· is concerned, by the following experiment. Five grams of methyl chlorocarbonate were added to 3 grams of acetylphenylthiocarbamide in a flask and the mixture heated on the water-bath under a reflux condenser for 20 minutes, until all solid had disappeared. Acetyl chloride, hydrogen chloride, and traces of hydrogen sulphide were evolved just as in the experiment made with ethyl chlorocarbonate. The contents of the flask solidified on pouring out into a dish, and the solid matter, when freed as far as possible from a rather sticky mother liquor (containing acetyl chloride, methyl acetate, and unchanged chlorocarbonate), and purified by recrystallisation from alcohol, was obtained in fine, white needles melting at 157—158°, and giving on analysis, S = 15·34 per cent. (calc. S = 15·25 per cent.). The interaction is represented by the equation:

$$\text{PhNH·CS·NH·CO·Me} + \text{MeO·COCl} = \text{PhNH·CS·NHCO·OMe} + \text{MeCOCl}.$$

Acetyl-*o*- and -*p*-tolylthiocarbamides give identical results under similar treatment; in fact, the method is probably a generic one, whereby thiocarbamides and thioureas containing the group R′O·CO· may be obtained from the corresponding acetyl compounds.

As disposing of all the work which he intends doing for the present with thiocarbimides derived from the chlorocarbonates of the *fatty* series, the author would briefly describe here the preparation and properties of certain derivatives of carboxyamylthiocarbimide.

The parent substance was obtained by slow interaction, at the ordinary temperature, between finely-powdered and well-dried potassium thiocyanate and carboxyamylchlorocarbonate dissolved in pure anhydrous benzene. The experiment extended over three months, air having access all the time through a capillary opening to the vessel in which it was made; but the admission of moisture was prevented, as far as possible, by a long column of calcium chloride in a drying tube.

At the end of this time, the clear solution (which left no appreciable solid residue on evaporation to dryness), whilst desulphurising copiously with alkaline lead and silver solutions, still reacted rather strongly for chlorine; but as there were obvious indications that decomposition had commenced, the experiment was stopped, the liquid filtered from the potassium chloride (formed in accordance with the

general equation already given) and excess of unchanged potassium thiocyanate. It was then divided into equal parts, and the following derivatives were prepared by adding the corresponding amines, in alcoholic solution, until no further sign of interaction was observed. Very poor yields were obtained, but these were quite sufficient for satisfactory identification:

ab-*Carboxyamylphenylthiocarbamide*, $C_5H_{11}O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5$. —Fine white needles from light petroleum, melting at 97—98°, without decomposition.

0·2036 gave 0·1790 $BaSO_4$. S = 12·08.

$C_{13}H_{18}O_2N_2S$ requires S = 12·04 per cent.

ab-*Carboxyamyl-o-tolylthiocarbamide*, $C_5H_{11}O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_7H_7$. —This compound also crystallises in fine, white needles, closely resembling the phenyl derivative and melting at 96—97° without decomposition.

0·2082 gave 0·1734 $BaSO_4$. S = 11·45.

$C_{14}H_{20}O_2N_2S$ requires S = 11·44 per cent.

Both these compounds gave the usual reactions with lead and silver salts characteristic of the class they represent. They are very freely soluble in benzene or hot alcohol, and moderately so in cold alcohol, from which they separate as oils on the addition of water, but are practically insoluble in cold light petroleum.

An attempt was made to prepare carboxyamylthiourea by passing dry ammonia through another portion of the solution, and a white, crystalline product was obtained melting at 56—57°, which in alcoholic solution desulphurised with neutral and ammoniacal silver nitrate, and gave a mirror of lead sulphide on boiling with alkaline lead tartrate. The mean of two sulphur determinations was, however, S = 9·702 per cent., as against 16·85 required for $CSN_2H_3{\cdot}CO_2{\cdot}C_5H_{11}$. The product is probably a mixture of this compound with amyl carbamate, resulting from interaction between ammonia and the unchanged amyl chlorocarbonate present, but the quantity obtained was too small to permit of their separation.

The two fully identified derivatives furnish an interesting example of the effect of the introduction of the higher alkyl group (C_5H_{11} in place of C_2H_5 or CH_3) on the melting point, for whilst the differences between the melting points of the phenyl and *o*-tolyl derivatives of carboxymethylthiocarbimide and carboxyethylthiocarbimide are 14° and 22° respectively, in the present case there is only a difference of 1°. They are sufficiently close, in fact, to suggest, if without analytical data, the barely possible accident of using the same amine for both preparations. When mixed, however, in equal portions, the melting

point of the two compounds (96—97° and 97—98°) drops smartly to 84°.

An attempt has been made to tabulate the melting points of the compounds described in this and the previous communication, and some interesting relationships have been observed, particularly amongst the isomeric thiocarbamides and thiocarbamates.

The author does not intend to deal with this portion of his subject at present, but hopes shortly to lay before the Society an account of some derivatives of ethoxalylthiocarbimide which have been prepared, and to extend the present research to the action of lead or other thiocyanates on phenyl chlorocarbonate.

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XCV.—*A Laboratory Method for the Preparation of Ethylene.*

By G. S. NEWTH.

THE common method for obtaining ethylene by means of alcohol and sulphuric acid, and all its attendant drawbacks of charring, frothing, and the simultaneous evolution of carbon dioxide and sulphur dioxide, are too well known to require more than a passing allusion. Even when pure alcohol is employed, the trouble is only lessened, not removed. All these inconveniences, however, may be entirely obviated by the simple plan of substituting tribasic phosphoric acid for the sulphuric acid.

The formation of *phosphovinic acid*, a compound analogous to *sulphovinic acid*, by the action of phosphoric acid upon alcohol, was observed by Lassaigne as far back as 1820 (*Ann. Chim.*, 13, 294).

The fact that under certain conditions ethylene is evolved by the action of phosphoric acid on alcohol was recorded by Pelouze (*Ann. Chim.*, 1833, 52, 37), who states that when the acid is very concentrated, having the consistency of thick syrup, and is mixed with one-fifth of its weight of alcohol, a brisk effervescence results, and there is produced a large quantity of "bicarburet of hydrogen"; "oil of wine," is also formed, and the mixture, he says, becomes dark-coloured owing to the separation of carbon in the form of black flocks.

Although, therefore, there is no new chemical decomposition involved in the process I am about to describe, so far as I am aware no one has previously developed a practical method for obtaining

ethylene in quantity based upon the action of phosphoric acid on alcohol.

The process may be carried out as follows: About 50 or 60 c.c. of syrupy phosphoric acid of sp. gr. 1·75 are placed in a small Wurtz flask of about 180 c.c. capacity. The flask is fitted with a cork carrying a thermometer and a dropping tube, the end of the latter being drawn out to a fine tube, and reaching to the bottom of the flask. Phosphoric acid of sp. gr. 1·75 boils at a temperature about 160°. It is heated in the flask and allowed to boil for a few minutes until its temperature reaches 200°, when ethyl alcohol is allowed to enter drop by drop. Ethylene is immediately disengaged, and by maintaining the temperature between 200° and 220° a continuous supply of the gas can be obtained even from so small an apparatus at the rate of 10 to 15 litres per hour. The gas should be conducted through a small Woulf's bottle (100 to 150 c.c. capacity) standing in a vessel of ice, in which an aqueous liquid collects containing a small quantity of ether, unde composed alcohol, and traces of an oily liquid—presumably the so-called "oil of wine," referred to by Pelouze. The gas which passes on is practically pure ethylene, and contains no trace of carbon dioxide, and of course no sulphur dioxide. It is absorbed completely by fuming sulphuric acid. There is no charring or separation of carbon in the reaction flask, for although the liquid assumes a brownish colour, it remains perfectly clear. The mixture does not evince any tendency to "froth up," hence the operation may be carried out in small vessels. The process appears to be continuous, and so long as the supply of alcohol is maintained, the operation will go on without attention for apparently an indefinite period. In one experiment, the action was allowed to continue for several hours a day for a whole week, during which time several hundred litres of ethylene had been generated by the same quantity, 50 c.c., of phosphoric acid.

It is noticed that after a few days the glass vessel shows signs of being acted on by the phosphoric acid; it is advisable, therefore, to protect the thermometer by wrapping the extremity of it in a strip of platinum foil.

Ordinary methylated spirit may be used instead of pure alcohol, but in this case the ethylene will contain more or less methyl ether mixed with it, which, however, can be dissolved out by water.

My experiments do not entirely confirm the results recorded by Pelouze; that is to say, under no conditions do I obtain any deposition of carbon. Even when alcohol is added to phosphoric oxide itself there is no indication of blackening, although there is a brisk evolution of ethylene. The gas which is given off under these circumstances, however, always contains appreciable quantities of a gaseous phosphorus compound, probably phosphine, which is readily

seen by passing the gas through silver nitrate solution. Whether the formation of this gas is due to the presence of impurities in the phosphoric oxide or not is a matter which is still under investigation; the immediate point is that even under these conditions no carbonisation takes place.

Glacial phosphoric acid appears to be quite incapable of converting alcohol into ethylene under conditions which are in any way comparable to those just mentioned.

Preparation of Methyl Ether.

By substituting methyl alcohol for ethyl alcohol in the foregoing process and maintaining the temperature between 200° and 210°, the gas which is evolved is practically pure methyl ether. Specimens of the gas collected over mercury were found to dissolve completely and rapidly in water. By passing the gas through a tube cooled to −30°, it was wholly condensed to a colourless liquid which boiled at −23·5°.

Preparation of Propylene.

By operating in a similar manner with propyl alcohol, propylene in a state of purity is readily obtained. When the normal alcohol is employed, the temperature necessary to bring about the reaction is about 250°, while with *iso*propyl alcohol the decomposition proceeds rapidly at 210°.

As in the former case, the liquid products of the action were collected in a bottle cooled by ice or by ice and salt, whilst the gas was condensed in a tube immersed in a bath of solid carbon dioxide and ether. The liquefied gas was found to boil between −41° and −38°. The gas from this boiling liquid was passed into bromine, in which it was rapidly absorbed, yielding propylene dibromide boiling at 141°. The liquid products of the action were found to consist of an aqueous solution of the alcohol employed, together with small and varying quantities of liquid hydrocarbons.

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XCVI.—*Condensation of Phenols with Esters of the Acetylene Series. Part V. Homologues of Benzo-γ-pyrone.*

By Siegfried Ruhemann.

As has been shown previously (Ruhemann and Stapleton, Trans., 1900, **77**, 1179; Ruhemann and Bausor, this vol., p. 470), the esters which are formed by the interaction of the sodium derivatives of phenol and the cresols may be condensed to benzo-γ-pyrone (1 : 4-benzopyrone) and its homologues. The extension of this research to thymol and carvacrol is recorded in this paper. With regard to the nomenclature of the benzopyrone compounds, I follow M. M. Richter's plan, in which the numbering of positions starts with the oxygen atom of the pyrone ring.

Ethyl β-Thymoxycinnamate, $C_6H_5\cdot C(O\cdot C_6H_3<^{C_3H_7\ [2]}_{CH_3\ [5]})\cdot CH\cdot CO_2\cdot C_2H_5$.

This compound is formed by dissolving sodium (1 at.) in an excess of hot thymol and adding to the hot dark solution ethyl phenylpropiolate (1 mol.). The reaction takes place with development of heat, and the product, when allowed to stand, solidifies to a dark resin. This dissolves on being agitated with dilute sulphuric acid and ether; the ethereal layer is then shaken with potash to remove the excess of thymol, and the ether evaporated. The dark residue which remains behind, on distillation in a vacuum, yields a yellowish, very viscous oil which boils at 218—219° under 12 mm. pressure. On analysis:

0·2074 gave 0·5930 CO_2 and 0·1384 H_2O. C = 77·97; H = 7·41.
$C_{21}H_{24}O_3$ requires C = 77·78; H = 7·40 per cent.

β-Thymoxycinnamic Acid, $C_6H_5\cdot C[O\cdot C_6H_3(CH_3)\cdot C_3H_7]:CH\cdot CO_2H$.—The ester is hydrolysed when boiled with alcoholic potash for 3 hours on the water-bath. On adding dilute sulphuric acid to the alkaline solution after evaporation of the alcohol, the thymoxycinnamic acid is precipitated in the form of a resinous product which solidifies on standing, and crystallises from dilute alcohol in colourless prisms. These begin to decompose at 130°, and at 138° melt with evolution of gas; they are insoluble in water, but dissolve readily in alcohol or ether. β-Thymoxycinnamic acid shows the same behaviour as its lower homologues; sulphuric acid does not effect its condensation to a derivative of 1 : 4-benzopyrone. On analysis:

0·2055 gave 0·5738 CO_2 and 0·1252 H_2O. C = 77·12; H = 6·77.
$C_{19}H_{20}O_3$ requires C = 77·03; H = 6·76 per cent.

The *silver* salt, obtained as a white precipitate on mixing the solution of the acid in ammonia with silver nitrate, is insoluble in water and melts at 100°. For analysis, it was dried in a vacuum over sulphuric acid.

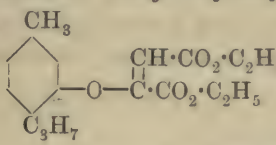
0·4675 left, on ignition, 0·1245 Ag. Ag = 26·63.
$C_{19}H_{19}O_3Ag$ requires Ag = 26·53 per cent.

β-Thymoxystyrene, $C_6H_5\cdot C(=CH_2)\cdot O\cdot {}^{[1]}C_6H_3{<}{}^{C_3H_7\ [2]}_{CH_3\ [5]}$.

On heating β-thymoxycinnamic acid, it loses carbon dioxide and yields β-thymoxystyrene. This distils at 177—178° under 10 mm. pressure as a colourless oil with a pleasant aromatic odour, and at 14°/14° has the density 0·9925. After standing for several weeks, it solidifies to a mass of crystals which melt at 26° and are very soluble in alcohol or ether. On analysis:

0·1967 gave 0·6170 CO_2 and 0·1405 H_2O. C = 85·55; H = 7·93.
$C_{18}H_{20}O$ requires C = 85·71; H = 7·94 per cent.

Action of the Sodium Derivatives of Thymol and Carvacrol on Ethyl Chlorofumarate. Ethyl Thymoxyfumarate,



The union of thymol with ethyl chlorofumarate takes place with development of heat when the unsaturated ester (1 mol.) is carefully added to the solution of sodium (1 at.) in an excess of thymol. The greenish, viscous product which is thus formed is allowed to stand overnight, and, after adding water and a little sulphuric acid, is extracted with ether. The ethereal solution is then freed from thymol by repeatedly shaking it with potash, the ether evaporated, and the residue distilled in a vacuum. The ester is a yellowish oil which boils at 194° under 10 mm. pressure, and at 14°/14° has the density 1·0493. On analysis:

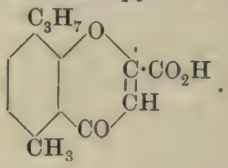
0·1997 gave 0·4940 CO_2 and 0·1372 H_2O. C = 67·46; H = 7·63.
$C_{18}H_{24}O_5$ requires C = 67·50; H = 7·50 per cent.

Thymoxyfumaric Acid, $C_3{}^{[2]}H_7\cdot({}^{[5]}CH_3)C_6H_3\cdot{}^{[1]}O\cdot C(CO_2H){:}CH\cdot CO_2H$.—

This acid is formed from the ester by boiling it with alcoholic potash for about 3 hours. After the alkaline solution has been freed from alcohol by distillation on the water-bath, water is added to the residue, and the solution acidified with dilute sulphuric acid. The solid which is thus precipitated, crystallises from hot dilute alcohol in yellowish needles which melt, not quite constantly, at 215° with evolution of gas, and are scarcely soluble in water. On analysis:

0·2010 gave 0·4680 CO_2 and 0·1115 H_2O. C = 63·50; H = 6·16.
$C_{14}H_{16}O_5$ requires C = 63·64; H = 6·06 per cent.

5-Methyl-8-propyl-1 : 4-benzopyrone-2-carboxylic Acid,

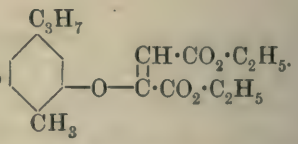


Thymoxyfumaric acid dissolves in cold concentrated sulphuric acid, forming a dark red solution. After standing for 24 hours, this is gradually poured into ice-cold water, when a white precipitate is formed which filters with difficulty, and crystallises from dilute alcohol in colourless, lustrous plates. These melt and decompose at 245°, and are freely soluble in alcohol or ether, but almost insoluble in water. On analysis:

0·2003 gave 0·5015 CO_2 and 0·1060 H_2O. C = 68·28; H = 5·88.
$C_{14}H_{14}O_4$ requires C = 68·29; H = 5·69 per cent.

The benzopyrone itself, which is formed on heating the acid, has not been further examined.

Ethyl Carvacroxyfumarate,



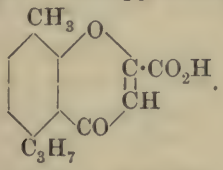
Sodium (1 at.) readily dissolves in an excess of hot carvacrol; on adding ethyl chlorofumarate (1 mol.) to the brown solution, heat is developed and the colour changes to green. The product is allowed to stand overnight, and, on proceeding as in the previous cases, the ethyl carvacroxyfumarate is obtained as a yellowish oil which distils at 206° under 14 mm. pressure, and at 14°/14° has the density 1·0445. On analysis:

0·2030 gave 0·5020 CO_2 and 0·1373 H_2O. C = 67·44; H = 7·51.
$C_{18}H_{24}O_5$ requires C = 67·50; H = 7·50 per cent.

The *acid*, $C_3\overset{[5]}{H}_7\cdot(\overset{[2]}{CH}_3)C_6H_3\cdot\overset{[1]}{O}\cdot C(CO_2H):CH\cdot CO_2H$, obtained from the ester on hydrolysis with alcoholic potash, is precipitated from the alkaline solution by means of dilute sulphuric acid as an oil which gradually solidifies. It crystallises from dilute alcohol in yellowish plates which melt at 175° with evolution of gas, and are readily soluble in alcohol or ether, but only sparingly so in water. On analysis:

0·1945 gave 0·4543 CO_2 and 0·1060 H_2O. C = 63·70; H = 6·05.
$C_{14}H_{16}O_5$ requires C = 63·64; H = 6·06 per cent.

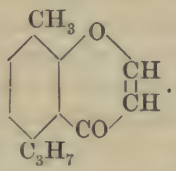
5-*Propyl*-8-*methyl*-1 : 4-*benzopyrone*-2-*carboxylic Acid*,



Carvacroxyfumaric acid dissolves in cold concentrated sulphuric acid, forming a red solution which, after standing overnight, is poured into cold water, when a white solid is precipitated; this crystallises from hot dilute alcohol in colourless prisms which melt and decompose at 237—238° and are readily soluble in alcohol or ether. On analysis:

0·2028 gave 0·5082 CO_2 and 0·1095 H_2O. C = 68·34; H = 6·00.
$C_{14}H_{14}O_4$ requires C = 68·29; H = 5·69 per cent.

5-*Propyl*-8-*methyl*-1 : 4-*benzopyrone*,



This compound is obtained by heating the acid; it distils as a yellowish oil which gradually solidifies. The solid contains, besides the benzopyrone, a small quantity of the acid, from which it is freed by shaking the ethereal solution of the distillate with potash. On allowing the ether to evaporate at the temperature of the room, the benzopyrone crystallises in colourless prisms which melt at 59—60°. On analysis:

0·2060 gave 0·5840 CO_2 and 0·1292 H_2O. C = 77·31; H = 6·97.
$C_{13}H_{14}O_2$ requires C = 77·23; H = 6·93 per cent.

Propylmethyl-1 : 4-benzopyrone has a pleasant odour and freely dissolves in alcohol or ether, but is insoluble in water; its solution in concentrated sulphuric acid has a faint greenish fluorescence.

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Cambridge.

XCVII.—*The colloid form of Piperine, with especial reference to its Refractive and Dispersive Powers.*

By Henry G. Madan, M.A.

Piperine, the alkaloid extracted from pepper by digestion with alcohol, appears to have attracted what little attention has been bestowed upon it rather from its chemical than from its physical properties. Wackenroder, however (quoted by Gmelin, *Handbook of Chemistry*, **15**, 18 *), observed that the crystallised substance, after being melted, solidified on cooling into a resinous, strongly refracting mass. More recently, this resinous form of piperine has been tried as a material for mounting objects for examination under the microscope, but it has not been found satisfactory, partly from an apparent want of permanency, but mainly because it is found to interfere with the definition of objects immersed in it. The reason of this will be evident from what is said in the latter part of this paper with reference to its dispersive power.

It seemed desirable, in the first place, to ascertain the exact conditions under which crystalloid piperine is converted into colloid piperine, and *vice versâ*. For this purpose, some of the ordinary substance, crystallised in monoclinic prisms, was placed in a beaker, and the latter was placed in an oil-bath maintained at a temperature of 180°. The crystals melted at 132°, and as soon as the whole was fully liquefied a portion of it was poured off upon a glass plate and marked "A." The beaker was replaced in the oil-bath and further heated. As soon as its contents had reached the temperature of the bath, namely, 180°, they were poured off upon another glass plate and labelled "B."

In both cases, A and B, the substance solidified to a light yellow, transparent resin (the colour of B being rather darker than that of A), without any sign of crystallisation. When cold, the mass was tough and slightly "tacky," receiving a faint indentation from the finger-nail. A small portion was detached from specimen A and heated slowly on a water-bath. At a temperature just below 100° it quickly

* The original paper appeared in *Archiv. des Apothekerverein im nördlichen Deutschland*, von Rud. Brandes, **37**, 349; a reference which I have not been able to verify.

lost its transparency, becoming a light yellow, nearly opaque mass resembling sulphur, which under the microscope was seen to consist of a network of interlacing crystals. This, when further heated, underwent no apparent change until the usual melting point, 132°, was reached, when it fused in the ordinary way and solidified as before into a transparent resin on cooling. The process of reheating and cooling was repeated more than once, with the same results.

A portion detached from specimen B was treated similarly and behaved in a precisely similar way.

The remainders of the preparations A and B were set aside under a bell-jar and examined from time to time. In about ten days, yellow, sulphur-like spots began to appear on the surface of A, and a little later in the interior of the mass also. These, when examined under the microscope, were found to consist of tufts of prismatic crystals, forming a very beautiful object in polarised light. They gradually extended, with the ultimate result that in about three months the surface was covered, and in about six months the whole mass had reverted to the crystalline condition.

With regard to preparation B, the same gradual change took place; perhaps rather more tardily than in the case of A, but with the same ultimate result.

Several similar sets of experiments have been made, which have only served to confirm the above observations.

It would appear, therefore, (1) that at a temperature only slightly, if at all, above its melting point crystalloid piperine is converted (for the most part, at any rate) into the colloid condition; (2) that the latter condition, when thus prepared, is not permanent, but reverts spontaneously, after the lapse of a moderate time, and quickly when exposed to a temperature of 100°, to the crystalloid form.

The closely analogous behaviour of sulphur will be at once recalled to mind. It is well known that octahedral sulphur (S_α), when heated to a temperature of 160° or higher, changes into the colloid form known as "plastic sulphur," or "S_γ," and that the latter, although it can be retained as such for a time by rapid cooling, reverts spontaneously in the course of a few days, and quickly when heated to a temperature a little below the usual melting point, to the original crystalloid form, S_α. A further important point bearing on these changes was observed by Frankenheim (*J. pr. Chem.*, 1840, **16**, 7), and also by Deville (*Ann. Chim. Phys.*, 1856, [iii], **47**, 111), namely, that during the heating of sulphur, at a certain point (or, perhaps, more than one point) of temperature a large amount of kinetic energy, supplied in the form of heat, is transferred to the sulphur molecules, in which it is stored up as some form of statical energy essential to the existence of the plastic condition. (In the phraseology of the

older physicists, "a large amount of heat becomes latent.") This energy reappears in a kinetic form (that of heat) when S_γ changes back into S_α. To quote one proof of the latter fact, Deville, experimenting with a mass of a kilogram or more of sulphur heated to 200°, and allowed to cool under uniform conditions, found that while the mass cooled from 170° to 165° in 50 seconds, and from 140° to 135° in 70 seconds, it took no less than 104 seconds to cool from 155° to 150°, and 125 seconds to cool from 150° to 145°, the endothermic supply serving to arrest the fall in temperature due to loss of heat by radiation and convection. Similarly, when a mass of sulphur was exposed to a uniform source of heat, the temperature did not rise at a uniform rate, but slackened while the transfer of energy to the molecules was taking place.

Now, it seemed very probable that something of the same kind might occur in the case of piperine, and that a prolonged continuance of the supply of heat might be necessary to ensure the complete conversion of the crystalloid into the colloid condition. The following experiments were made with the view of ascertaining whether this was the case.

Some crystallised piperine was placed in a beaker immersed in an oil-bath maintained at a constant temperature of 180°. When the liquefied substance had attained the temperature of the bath, a small portion was poured off on to a glass plate, labelled "C," and reserved for comparison. The remainder was maintained at 180° for one hour, near the end of which time it became slightly viscous. The colour also darkened to a full yellow (orange in thick layers), probably owing to the separation of a trace of carbon at the high temperature, since at 200° a perceptible amount of decomposition takes place. At the expiration of an hour, the whole was poured off and allowed to cool on a plate labelled "D." When it was cold, a small piece was broken off and gradually heated on a slip of glass. It did *not* crystallise at 100°, nor did it undergo any change until the usual melting point (132°) was reached, when it became viscous, but did not attain sufficient fluidity to be poured out until the temperature reached 170° or nearly so. It was allowed to cool and again heated, and this was repeated three or four times, but not a trace of crystallisation was observed. A portion of the preparation "C," when treated in the same way, became crystalline at 100°, like the preparation "B" already described. The remainders of both preparations, "C" and "D," were kept under a bell-jar and examined from time to time.

These experiments were made in October, 1898, and in about a fortnight "C" was spotted with yellow; it passed altogether into the crystalline condition in about the usual time—six months. No change whatever was noticed in preparation "D," although its surface

was scratched to promote crystallisation if possible; and up to the present time, more than two and a-half years since its preparation, it has remained quite unaltered, closely resembling ordinary "rosin" (colophony) in appearance, but not quite so brittle.

The inference which we seem entitled to draw from the results of the above experiments (and other similar ones, which corroborate them) is, that in order to ensure with even approximate certainty the conversion of crystalloid piperine into colloid piperine, an exposure to a temperature of not much less than 180° for a period of not much less than one hour is required. Whether even then the tendency to revert to the crystalline condition is entirely overcome, time alone can show.

I may mention that I have made similar experiments with quinidine, and found it to behave in a similar way. It passes, when heated for an hour to 180°, into a permanent (as far as hitherto observed) colloid, having a rather high refractivity ($\mu_D = 1{\cdot}602$).

The Refractive and Dispersive Powers of Piperine.

For the purpose of determining these, a hollow prism was made by cementing thin glass plates (selected with parallel surfaces) to the sides of a prism of dense flint glass. The height of the glass plates was rather more than twice that of the prism, so that they formed above the latter a cell of about the same size and having the same angles. This cell was filled with melted piperine, and thus a double prism was obtained, the lower part of dense flint glass and the upper part of piperine, with a refracting angle common to both. This was mounted in a brass frame with levelling screws for adjustment on the table of the spectrometer.

In the first place, the refracting angle was determined in the usual way; the mean of several concordant sets of readings giving $\alpha = 24°10'10''$. Then the angle of minimum deviation (δ) for each of the principal lines of the spectrum was observed, both for the piperine prism and the glass one below it, and the corresponding indices of refraction were calculated by the usual formula,

$$\mu = \sin\tfrac{1}{2}(\alpha + \delta)/\sin\tfrac{1}{2}\alpha.$$

The results are given in the table on p. 926.

It will be evident from the figures given in the table that colloid piperine possesses a higher refractivity than most, perhaps all, other resins or resin-like substances, the only one which comes at all near it, so far as I know, being naphthyl phenyl ketone (*Phil. Mag.*, 1886, [v], 21, 245) (for which $\mu_D = 1{\cdot}669$) and the compound which it forms with bromine.

Indices of refraction of piperine and of dense flint glass.

Spectrum-line.	Piperine.	Glass.
K_α	1·631	1·758
*H_α (C)	1·667	1·766
†D	1·684	1·774
E	1·710	1·784
H_β (F)	1·738	1·795
H_γ	1·810	1·806
Coefficient of dispersion ($\mu_{H\gamma} - \mu_{H\alpha}$)	0·143	0·040

* For the observation of the hydrogen-lines, one of the "end on" vacuum tubes devised by Prof. Piazzi Smyth was used, in which the light from a considerable thickness of glowing hydrogen is passed through the slit, and a very brilliant spectrum is obtained.

† The only other determination of the refractivity of piperine which I have been able to find is one by Dr. P. Riedel of Jena, quoted in Behrens' "Tabellen," (1st edition); and he only gives one index, namely, $\mu_D = 1{\cdot}6844$, an agreement sufficiently close to promote confidence in my own results.

The above determinations were made with piperine which had not been heated for the full period of an hour. From experiments very recently made, it would seem that prolonged heating perceptibly diminishes the refractivity of the material.

The dispersive power of piperine is still more remarkable, being probably as great as, if not greater than, that of any other known substance. The coefficients of dispersion (taken as $\mu_{H\gamma} - \mu_{H\alpha}$) of a few substances are as follows:

Piperine	0·142	Carbon disulphide	0·057
Phosphorus	0·106	α-Monobromonaphthalene	0·051
Methylene diiodide	0·062	Dense flint glass	0·040
Phenylthiocarbimide	0·060		

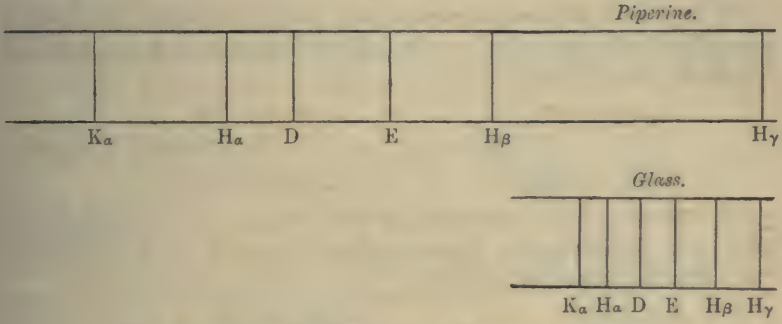
and it is obvious that piperine is far ahead of the others.

The diagram given on p. 927 shows the extent of the piperine spectrum as compared with that given by a prism of dense flint glass having the same refracting angle. In the original drawing, 1 mm. was taken to represent 1′ of arc.

It will be noticed that while piperine has almost exactly the same refractive power as dense flint glass for H_γ in the blue, the refractive indices for rays of greater wave-length differ widely in the two substances, the result being that the visible spectrum given by piperine is nearly four times the length of that given by flint glass.

From the high refractivity of piperine, it seemed likely to be useful in the construction of certain kinds of polarising prisms. It would be

hardly appropriate to enter into details here, but I may say that besides the usual type of nicol prism in which the extraordinary ray is transmitted while the ordinary ray is got rid of by total reflection, there is another class of polarising prisms made of Iceland spar, in which the ordinary ray is transmitted, the extraordinary ray being the one which is turned aside by total reflexion and abolished. For the latter class, of which the prisms devised by Jamin and by Bertrand may be taken as examples, a medium is required which shall have the same refractive index as that of Iceland spar for the ordinary ray, namely, 1·658. Now, although the refractivity of piperine is above this, it can easily be reduced to the proper level by admixture



Comparative length of the spectra of piperine and glass.

with Canada balsam. In fact, I have a prism of this kind in which such a mixture (piperine, 4 parts; balsam, 1 part) replaces the usual balsam film. Unfortunately, however, owing to the extraordinarily high dispersive power of piperine, the critical angles for the different rays of the visual spectrum differ so widely that the prism is practically useless unless monochromatic light is employed.

Still, it would be easy to mention other purposes for which a medium of high dispersive power is useful, and it may be of some service to have called attention to the eminent degree in which piperine possesses this property.

XCVIII.—*The Condensation of Phenyl Ethyl Ketone and Benzaldehyde.*

By Robert Duncombe Abell, B.Sc. (Wales), 1851 Exhibition Scholar of the University College of North Wales, Bangor.

Acetophenone condenses with benzaldehyde in three proportions:

(i) One mol. of acetophenone with 1 mol. of benzaldehyde, to form an unsaturated ketone, benzalacetophenone (Claisen and Claparède, *Ber.*, 1881, **14**, 2464; Claisen *Ber.*, 1887, **20**, 655).

$$C_6H_5\cdot CO\cdot CH_3 + C_6H_5\cdot CHO = H_2O + C_6H_5\cdot CO\cdot CH{:}CH\cdot C_6H_5.$$

(ii) Two mols. of acetophenone with 1 mol. of benzaldehyde, to form benzaldiacetophenone or 2-phenyl-1:3-dibenzoylpropane (Kostanecki and Rossbach, *Ber.*, 1896, **29**, 1492).

$$\begin{matrix} C_6H_5\cdot CO\cdot CH_3 \\ \qquad O{:}CH\cdot C_6H_5 \\ C_6H_5\cdot CO\cdot CH_3 \end{matrix} = \begin{matrix} C_6H_5\cdot CO\cdot CH_2 \\ \quad | \\ CH\cdot C_6H_5 \\ \quad | \\ C_6H_5\cdot CO\cdot CH_2 \end{matrix} + H_2O.$$

(iii) Three mols. of acetophenone with 2 mols. of benzaldehyde, to form two stereoisomeric dibenzaltriacetophenones or 2:4-diphenyl-1:3:5-tribenzoylpentanes (*ibid.*).

$$\begin{matrix} C_6H_5\cdot CO\cdot CH_3 \\ \qquad O{:}CH\cdot C_6H_5 \\ C_6H_5\cdot CO\cdot CH_3 \\ \qquad O{:}CH\cdot C_6H_5 \\ C_6H_5\cdot CO\cdot CH_3 \end{matrix} = \begin{matrix} C_6H_5\cdot CO\cdot CH_2 \\ \quad | \\ CH\cdot C_6H_5 \\ \quad | \\ C_6H_5\cdot CO\cdot CH \\ \quad | \\ CH\cdot C_6H_5 \\ \quad | \\ C_6H_5\cdot CO\cdot CH_2 \end{matrix} + 2H_2O.$$

Ketones of the form $R\cdot CO\cdot CH_2\cdot R'$, for example, phenyl ethyl ketone, $C_6H_5\cdot CO\cdot CH_2\cdot CH_3$, do not undergo this third form of condensation.

The property of condensation is intimately associated with the group $-CO\cdot CH_2-$, the hydrogen atoms of which are slightly electronegative in character.

The formation of the preceding compounds may be regarded as taking place in the following manner:

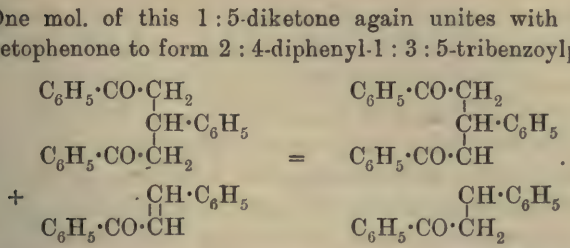
(i) One mol. of acetophenone condenses with 1 mol. of benzaldehyde to form benzalacetophenone.

$$C_6H_5\cdot CO\cdot CH_3 + C_6H_5\cdot CHO - H_2O = C_6H_5\cdot CO\cdot CH{:}CH\cdot C_6H_5.$$

(ii) One mol. of benzalacetophenone then unites with 1 mol. of acetophenone to form 2-phenyl-1:3-dibenzoylpropane.

$$\begin{matrix} C_6H_5\cdot CO\cdot CH \\ \quad \| \\ \qquad CH\cdot C_6H_5 \\ + C_6H_5\cdot CO\cdot CH_3 \end{matrix} = \begin{matrix} C_6H_5\cdot CO\cdot CH_2 \\ \quad | \\ CH\cdot C_6H_5. \\ \quad | \\ C_6H_5\cdot CO\cdot CH_2 \end{matrix}$$

(iii) One mol. of this 1 : 5-diketone again unites with 1 mol. of benzalacetophenone to form 2 : 4-diphenyl-1 : 3 : 5-tribenzoylpentane.

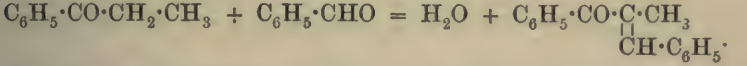


In the first and second reactions the group $-CO\cdot CH_2-$ is present in the acetophenone taking part in these reactions, whereas in the third reaction this group is present in the 1 : 5-diketone.

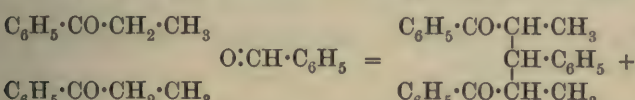
If now phenyl ethyl ketone, $C_6H_5\cdot CO\cdot CH_2\cdot CH_3$, take the place of acetophenone, this substance also contains the group $-CO\cdot CH_2-$, and consequently reactions corresponding to i and ii are to be expected, but not the third reaction, because the 1 : 5-diketone, 2-phenyl-1 : 3-dimethyl-1 : 3-dibenzoylpropane, $C_6H_5\cdot CO\cdot CH(CH_3)\cdot CH(C_6H_5)\cdot CO\cdot CH(CH_3)\cdot C_6H_5$, which we should expect to be formed in the second reaction, would no longer contain this group.

It was therefore expected that benzaldehyde and phenyl ethyl ketone would condense in two proportions :

(i) One mol. of phenyl ethyl ketone with 1 mol. of benzaldehyde to form the unsaturated ketone, benzalpropiophenone, or benzalmethylacetophenone :



(ii) Two mols of phenyl ethyl ketone with 1 mol. of benzaldehyde to form one or more stereoisomeric 1 : 5-diketones, for example :



The following experiments were undertaken with the view of investigating these reactions. Mixtures of phenyl ethyl ketone and benzaldehyde were treated with the following reagents :

Sodium methoxide, 20 per cent. solution.

Sodium ethoxide, 20 per cent. solution.

Potassium hydroxide in aqueous alcoholic solution.

Dry hydrogen chloride.

Condensation of Phenyl Ethyl Ketone and Benzaldehyde by means of a 20 per cent. solution of Sodium Methoxide.

A mixture of 5 grams of benzaldehyde and 6·3 grams of phenyl ethyl ketone was treated with 15 c.c. of a 20 per cent. solution of sodium methoxide. After standing for 7 days, the gelatinous, yellow mass was dissolved by shaking with ether and dilute hydrochloric acid. The ethereal solution was washed with a dilute solution of sodium hydroxide and afterwards with water, and was then dried over fused sodium sulphate. After distilling off the ether, a clear oil remained which was distilled under 25 mm. pressure, until the thermometer rose rapidly to 200°. A fraction boiling at 95—120° consisting of unchanged benzaldehyde and phenyl ethyl ketone was collected separately. As soon as the thermometer registered 200°, the oil distilling over began to solidify. The distillation was then stopped, the residue in the flask washed out with dry ether, and the ether evaporated off in a current of dry air. The oil which was thus obtained crystallised almost completely on standing for a few hours in a vacuum over sulphuric acid.

(1) *Examination of the Crystalline Portion of the Condensation Product.*—The crystalline mass was triturated with cold light petroleum which dissolved out an oil leaving behind a mass of fine crystals melting at 92—96°. This substance, upon repeated recrystallisation from large quantities of boiling light petroleum, to which a few drops of alcohol had been added, separated in needles melting at 98—99°. It is easily soluble in alcohol, benzene, chloroform, acetone, or ether, but only very sparingly so in boiling light petroleum. On analysis:

0·2 gave 0·581 CO_2 and 0·1345 H_2O. C = 79·22; H = 7·47.
0·2012 „ 0·5845 CO_2 „ 0·1355 H_2O. C = 79·21; H = 7·48.
C_8H_9O requires C = 79·33; H = 7·44 per cent.

Determinations of the molecular weight by the boiling point method gave the following results:

0·2992 dissolved in 29·16 chloroform gave a rise of temperature 0·158°. Mol. wt. = 238.
0·5192 dissolved in 29·16 chloroform gave a rise of temperature 0·258°. Mol. wt. = 252.
Mean = 245.—$C_{16}H_{18}O_2$ has mol. wt. = 242.

The substance is not acted on by potassium permanganate or bromine and is therefore saturated. Further, it cannot contain a ketonic or an aldehydic group because it does not react with phenylhydrazine, hydroxylamine, &c.

Diacetyl Derivative, $C_{16}H_{16}(O{\cdot}CO{\cdot}CH_3)_2$.—Two grams of the sub-

stance were boiled with 2 grams of fused sodium acetate and 20 grams of acetic anhydride for 4 hours. The oil which first separated on treatment with water rapidly became crystalline and after recrystallisation from alcohol, formed prisms melting at 123—124°. On analysis:

0·2005 gave 0·541 CO_2 and 0·124 H_2O. C = 73·61; H = 6·86.
0·202 „ 0·545 CO_2 „ 0·1232 H_2O. C = 73·57; H = 6·77.
$C_{20}H_{22}O_4$ requires C = 73·62; H = 6·74 per cent.

The substance, is therefore, the diacetyl derivative of $C_{16}H_{18}O_2$, which is thus proved to contain two hydroxyl groups.

Oxidation of Substance $C_{16}H_{18}O_2$ (m. p. 98—99°).—When heated with a mixture of potassium dichromate and sulphuric acid, this substance is oxidised to benzoic and carbonic acids.

One gram of the compound was next dissolved in 40 grams of glacial acetic acid and oxidised at the boiling point with 0·6 gram of chromic acid, added in small quantities at a time. The green solution so obtained was precipitated with water, and the precipitate extracted with ether. The ethereal solution, after being washed with sodium hydroxide and then with water, was dried over fused sodium sulphate and the ether evaporated off in a current of dry air. An oil remained which readily crystallised, and after recrystallisation from alcohol was obtained in needles melting at 82·5—84°. On analysis:

0·1717 gave 0·5072 CO_2 and 0·0922 H_2O. C = 80·54; H = 5·96.
0·2005 „ 0·5925 CO_2 „ 0·108 H_2O. C = 80·59; H = 5·98.
$C_{16}H_{14}O_2$ requires C = 80·67; H = 5·88 per cent.

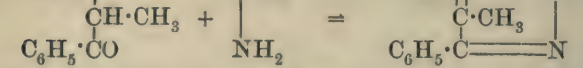
The oxidation product (0·5 gram) being in all probability a ketone or an aldehyde, was dissolved in alcohol, and mixed with a 50 per cent. solution of hydrazine hydrate (0·3 gram). After standing for 12 hours, the solution was precipitated with water, and the precipitate, after recrystallisation from alcohol, was obtained in glistening plates melting at 222—223°. It was dried at 120° and analysed:

0·2022 gave 21·7 c.c. nitrogen at 16° and 740 mm. N = 12·12.
$C_{16}H_{14}N_2$ requires N = 11·96 per cent.

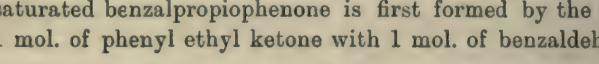
The compound $C_{16}H_{14}O_2$ (m. p. 82·5—84°), and the compound $C_{16}H_{14}N_2$ (m. p. 222—223°), are therefore identical with the methyldibenzoylmethane and the 3 : 5-diphenyl-4-methylpyrazole obtained by Beyme (*Diss. Leipzig*, 1900). From this it follows that the methyldibenzoylmethane is obtained from the corresponding 1 : 3-disecondary alcohol, namely, 1·3-diphenyl-2-methyltrimethylene glycol, for example:

$$\begin{array}{l} C_6H_5\cdot CH\cdot OH \\ \quad\quad | \\ \quad CH\cdot CH_3 \\ \quad\quad | \\ C_6H_5\cdot CH\cdot OH \end{array} + 2O = \begin{array}{l} C_6H_5\cdot CO \\ \quad\quad | \\ \quad CH\cdot CH_3 \\ \quad\quad | \\ C_6H_5\cdot CO \end{array} + 2H_2O.$$

The methyldibenzoylmethane being a 1 : 3-diketone, reacts with hydrazine to form 3 : 5-diphenyl-4-methylpyrazole, for example :

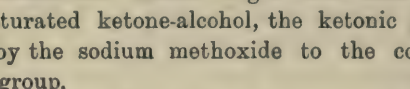


The formation of 1 : 3-diphenyl-2-methyltrimethylene glycol is remarkable, but may be explained on the assumption that the unsaturated benzalpropiophenone is first formed by the condensation of 1 mol. of phenyl ethyl ketone with 1 mol. of benzaldehyde, thus :



This unsaturated ketone might then take up a mol. of water to form a saturated ketone-alcohol, the ketonic group being afterwards reduced by the sodium methoxide to the corresponding secondary alcoholic group.

It is scarcely possible that the reduction of the ketonic group takes place before the elements of water have been taken up by the benzalpropiophenone to form a saturated compound, because the double bond would in all probability be first attacked by the nascent hydrogen and one or more of the following compounds would be formed :



none of which has been found in the crystalline part of the product of the original condensation, but may be present in the solution of the oily part in light petroleum.

(2) *Examination of the Oily Portion of the Condensation Product.*— The solution of the oil in light petroleum was dried by means of fused sodium sulphate, the solvent distilled off, and the residual oil distilled under reduced pressure. The fraction boiling at 210—213° under 23 mm. pressure formed a clear, yellowish oil which furnished the following results upon analysis :

0·2175 gave 0·6742 CO_2 and 0·1287 H_2O. C = 84·54 ; H = 6·57.
0·2 „ 0·621 CO_2 „ 0·1197 H_2O. C = 84·68 ; H = 6·65.

These figures do not agree with those required by benzalpropiophenone, $C_{16}H_{14}O$ (C = 86·48 ; H = 6·31 per cent.).

The oil, however, has an unsaturated constitution, since it readily absorbs bromine. It is therefore probably benzalpropiophenone containing a small quantity of the 1 : 3-disecondary alcohol which boils at about the same temperature (the pressure being the same in the two cases), or the impurity may consist of small quantities of other pro-

ducts of the reaction which cannot be separated from the benzalpropiophenone by distillation.

On comparison of the figures with those required by the formulæ of the various products which might result from the reaction, it will be seen that they agree most closely with the figures for benzalpropiophenone.

The figures are here given for comparison:

$C_6H_5\cdot CO\cdot C(CH_3){:}CH\cdot C_6H_5$ requires C = 86·48 ; H = 6·31.

$C_6H_5\cdot CH(OH)\cdot C(CH_3){:}CH\cdot C_6H_5$
$C_6H_5\cdot CO\cdot CH\cdot(CH_3)\cdot CH_2\cdot C_6H_5$ } ,, C = 85·72 ; H = 7·14.

$C_6H_5\cdot CH(OH)\cdot CH(CH_3)\cdot CH_2\cdot C_6H_5$,, C = 84·96 ; H = 7·96.

Found (mean) C = 84·61 ; H = 6·61.

This conclusion is confirmed by the reaction of benzalpropiophenone with phenyl ethyl ketone described on p. 936.

Condensation of Phenyl Ethyl Ketone and Benzaldehyde by means of a 20 per cent. solution of Sodium Ethoxide.

A mixture of 5 grams of benzaldehyde and 6·2 grams of phenyl ethyl ketone was treated with 15 c.c. of a 20 per cent. solution of sodium ethoxide. After standing for 7 days, the hard, pink-coloured product was shaken up with ether and dilute hydrochloric acid, when a small quantity of a crystalline compound melting at 160—163° remained undissolved. This substance, after recrystallisation from alcohol, melted at 162—163°.

The ethereal solution was treated in the same way as that obtained from the condensation by means of sodium methoxide and contained:

i. Unchanged benzaldehyde and phenyl ethyl ketone.

ii. 1 : 3-Diphenyl-2-methyltrimethylene glycol, $C_{16}H_{18}O_2$ (m. p. 98—99°), crystallising in needles.

iii. A yellowish oil boiling at 210—213° under 23 mm. pressure. This was analysed, with the following results:

0·206 gave 0·6435 CO_2 and 0·1227 H_2O. C = 85·19 ; H = 6·62.

0·206 ,, 0·6415 CO_2 ,, 0·1242 H_2O. C = 84·92 ; H = 6·69.

$C_{16}H_{14}O$ requires C = 86·48 ; H = 6·31 per cent.

This oil readily absorbs bromine and is consequently slightly impure benzalpropiophenone as in the preceding case. For further proof of this conclusion, see p. 935.

iv. A compound crystallising in small, six-sided crystals melting at 162—163°, which furnished the following results on analysis:

0·201 gave 0·621 CO_2 and 0·1245 H_2O. C = 84·25 ; H = 6·88.

0·2005 ,, 0·619 CO_2 ,, 0·1235 H_2O. C = 84·19 ; H = 6·84.

$C_{25}H_{24}O_2$ requires C = 84·27 ; H = 6·74 per cent.

This substance is obviously 2-phenyl-1 : 3-dimethyl-1 : 3-dibenzoylpropane, formed by the condensation of 2 mols. of phenyl ethyl ketone and 1 mol. of benzaldehyde with separation of 1 mol. of water (p. 929).

To test the correctness of this view, a mixture of 5 grams of benzaldehyde (1 mol.) and 12·6 grams of phenyl ethyl ketone (2 mols.) was treated with 15 c.c. of a 20 per cent. solution of sodium ethoxide, with the result that the compound $C_{25}H_{24}O_2$ (m. p. 162—163°) was obtained in slightly greater quantity.

The preparation of pure benzalpropiophenone was next attempted, potassium hydroxide or hydrogen chloride gas being used as the condensing agent.

Condensation of Phenyl Ethyl Ketone and Benzaldehyde by means of Potassium Hydroxide.

A mixture of 12·6 grams of phenyl ethyl ketone and 10 grams of benzaldehyde was dissolved in 100 c.c. of alcohol, and 3—4 c.c. of a concentrated aqueous solution of potassium hydroxide were added; the whole was diluted with water, but not in such quantity as to precipitate the ingredients, and the mixture allowed to stand for 7 days. A small quantity of a yellowish oil separated. The aqueous alcoholic solution was precipitated with water and extracted with ether. The ethereal solution, dried by means of fused sodium sulphate, was evaporated, and the remaining oil distilled under 22 mm. pressure and collected in the following fractions:

i. Benzaldehyde, b. p. 85—88° (185—190° under atmospheric pressure).

ii. Phenyl ethyl ketone, b. p. 103—108° (210—215° atmospheric pressure).

iii. A yellowish unsaturated oil, b. p. 200—220°.

The last portion was redistilled a number of times, and the portion boiling at 210—213° under 23 mm. pressure analysed:

0·2175 gave 0·685 CO_2 and 0·1227 H_2O. C = 86·35; H = 6·27.
$C_{16}H_{14}O$ requires C = 86·48; H = 6·31 per cent.

Benzalpropiophenone can therefore be prepared pure by this method, but the yield (10 per cent. of the theoretical) is small.

Condensation of Phenyl Ethyl Ketone and Benzaldehyde by means of Hydrogen Chloride.

When a mixture of molecular quantities of phenyl ethyl ketone and benzaldehyde is treated with dry hydrogen chloride until 1 mol. has been absorbed, a dark oil is obtained which readily splits off hydrogen chloride, and from which no definite chlorine compound could be

isolated. This oil after being kept for 12 hours in a closed vessel was gently heated on a sand-bath in a current of air until it no longer gave off hydrogen chloride, and was then distilled under reduced pressure. The fraction boiling at 234—235° under 25 mm. pressure, which still contained chlorine, was analysed with the following results:

0·2345 gave 0·6985 CO_2 and 0·1275 H_2O. C = 84·85; H = 6·31.
0·232 „ 0·7267 CO_2 „ 0·13 H_2O. C = 85·43; H = 6·22.
0·4632 „ 0·0239 AgCl. Cl = 1·27.
0·4947 „ 0·02714 AgCl. Cl = 1·35.
$C_{16}H_{15}OCl$ requires C = 74·29; H = 5·80; Cl = 13·73 per cent.
$C_{16}H_{14}O$ „ C = 86·48; H = 6·31 per cent.

From these figures it is evident that about nine-tenths of the chlorine has been eliminated by heating, one-tenth still remaining after a number of distillations. It is therefore probable that in the reaction two isomeric compounds are formed, and that one of these is much less stable than the other. The remaining chlorine can be removed as hydrochloric acid by boiling the substance with an aqueous 50 per cent. solution of potassium hydroxide.

Benzalpropiophenone so obtained is straw-yellow and distils without decomposition at 210—213° under 23 mm. pressure; the yield amounts to 70—80 per cent. of the theoretical. It was analysed with the following results:

0·2122 gave 0·6732 CO_2 and 0·122 H_2O. C = 86·50; H = 6·38.
0·209 „ 0·6625 CO_2 „ 0·119 H_2O. C = 86·45; H = 6·32.
$C_{16}H_{14}O$ requires C = 86·48; H = 6·31 per cent.

The *phenylhydrazone*, crystallised from alcohol in yellow needles softening at 115° and melting at 127—128°. On analysis:

0·2012 gave 0·6235 CO_2 and 0·1185 H_2O. C = 84·49; H = 6·53.
0·2005 „ 16 c.c. nitrogen at 20° and 752 mm. N = 9·03.
$C_{22}H_{20}N_2$ requires C = 84·61; H = 6·41; N = 8·97 per cent.

Benzalpropiophenone dibromide, $C_6H_5{\cdot}CO{\cdot}CBr(CH_3){\cdot}CHBr{\cdot}C_6H_5$. —Ten grams of benzalpropiophenone were dissolved in 80 grams of chloroform, and 7·3 grams of bromine in 20—30 grams of chloroform gradually added to the solution. The bromine was rapidly decolorised with a slight development of heat, and only a small quantity of hydrogen bromide was evolved. The product was at once poured into an evaporating dish, the chloroform evaporated in a current of dry air, and the thick viscid oil placed over sulphuric acid and potassium hydroxide in a vacuum until the weight was constant. The green viscous oil thus obtained did not crystallise even after long standing, or when cooled with a mixture of solid carbonic acid and ether. On analysis:

0·232 gave 0·428 CO_2 and 0·0797 H_2O. C = 50·31 ; H = 3·81.
0·2515 „ 0·4642 CO_2 „ 0·0865 H_2O. C = 50·34 ; H = 3·82.
0·327 „ 0·3205 AgBr. Br = 41·75.
0·2792 „ 0·273 AgBr. Br = 41·60.
$C_{16}H_{14}OBr_2$ requires C = 50·26 ; H = 3·66 ; Br = 41·89 per cent.

In the various preparations of the dibromide, the amount of bromine present was found to vary between 38 and 43 per cent.

Condensation of Benzalpropiophenone with Phenyl Ethyl Ketone.

It seemed probable that for the satisfactory preparation of 2-phenyl-1 : 3-dimethyl-1 : 3-dibenzoylpropane, the previous formation of the unsaturated benzalpropiophenone is necessary. The following experiments were therefore made.

A mixture of 4·4 grams of benzalpropiophenone and 2·7 grams of phenyl ethyl ketone was therefore treated with a solution of 0·5 gram of sodium in the least possible quantity of absolute alcohol. The mixture rapidly became pink in colour, with development of heat; crystals soon began to form, and in 48 hours the whole had solidified to a compact, crystalline mass. This was triturated with dilute alcohol, filtered, and washed with alcohol, when a nearly white, crystalline mass melting at 158—160° was obtained, which after recrystallisation from alcohol melted at 162—163°. It was almost insoluble in hot light petroleum, and only sparingly soluble in boiling alcohol and in ether. The yield of 2-phenyl-1 : 3-dimethyl-1 : 3-dibenzoylpropane was almost quantitative.

From the alcoholic mother liquors, a small quantity of a compound much more soluble in alcohol was obtained. This crystallised in needles and melted at 121—122°. On analysis:

0·2005 gave 0·6165 CO_2 and 0·1225 H_2O. C = 83·85 ; H = 6·78.
0·2015 „ 0·6202 CO_2 „ 0·123 H_2O. C = 83·96 ; H = 6·78.
$C_{25}H_{24}O_2$ requires C = 84·27 ; H = 6·74 per cent.

As the analyses show, this compound is isomeric with 2-phenyl-1 : 3-dimethyl-1 : 3-dibenzoylpropane (m. p. 162—163°). The yield amounts to 1 gram from reactions yielding upwards of 60 grams of the isomeride.

The mode of formation of these compounds, more especially of that of the higher melting point, by the above method indicates not only that they are isomeric 1 : 5-diketones, but is also a further proof of the unsaturated constitution of benzalpropiophenone.

Similar reactions of unsaturated compounds with substances which contain electro-negative hydrogen atoms have been carried out by Michael (*J. pr. Chem.*, 1887, [ii], **35**, 349), who studied, amongst other

reactions, the behaviour of ethyl cinnamate with the sodium derivatives of ethyl malonate and ethyl acetoacetate.

In the above case also, the union of the unsaturated ketone benzalpropiophenone with phenyl ethyl ketone follows in the sense of Michael's "positive-negative" rule (*J. pr. Chem.*, 1888, [ii], 37, 522), according to which "in the union of a sodium compound with an unsaturated compound, the sodium atom, replacing a hydrogen atom of the acid methylene ($=CH_2$) group, links itself to the carbon atom (of the unsaturated compound) which has the strongest negative character," in this case to the carbon atom attached to benzoyl on the one side and to methyl on the other in the radicle, $C_6H_5\cdot CO\cdot \overset{\|}{C}\cdot CH_3$. Consequently, the reaction may be represented by the following equation:

$$\begin{array}{rcl} C_6H_5\cdot CO\cdot \overset{\|}{C}\cdot CH_3 & & C_6H_5\cdot CO\cdot \overset{|}{C}Na\cdot CH_3 \\ \quad\quad CH\cdot C_6H_5 & = & \quad\quad\;\; \overset{|}{C}H\cdot C_6H_5. \\ + \quad C_6H_5\cdot CO\cdot CHNa\cdot CH_3 & & C_6H_5\cdot CO\cdot \underset{|}{C}H\cdot CH_3 \end{array}$$

The sodium compound so formed is then probably decomposed by the alcohol with regeneration of sodium ethoxide.

In carrying out this reaction, it is necessary to use an amount of sodium in agreement with the above equation in order to obtain the best results, and under these conditions the yield of 1:5-diketone is almost quantitative.

Again, in this reaction it was found that methyl alcohol cannot take the place of ethyl alcohol. This explains how it is that the 1:5-diketone is formed when phenyl ethyl ketone and benzaldehyde are condensed by means of sodium ethoxide, and not when sodium methoxide is used.

As this reaction is practically quantitative, it can be used to ascertain whether the oils boiling at 210—213° under 23 mm. pressure, obtained by the condensation of phenyl ethyl ketone and benzaldehyde by means of sodium methoxide and sodium ethoxide respectively, consist of benzalpropiophenone, as previously concluded.

2·2 grams of each of these oils were mixed with 1·3 grams of phenyl ethyl ketone and treated with 0·23 gram of sodium dissolved in absolute alcohol. The yield of 1:5-diketone was 3·3 grams, instead of 3·5 grams, that is 94 per cent. of the calculated amount in both cases, thus furnishing conclusive evidence that these oils are almost pure benzalpropiophenone.

In order to investigate further the structure of the isomerides, $C_{25}H_{24}O_2$, the reaction with ammonia and with hydroxylamine was studied in the hope of obtaining one and the same pyridine derivative by means of the following reaction:

$$\begin{array}{l} CH_3\cdot \underset{|}{C}H\cdot CO\cdot C_6H_5 \\ C_6H_5\cdot \underset{|}{C}H \\ CH_3\cdot \underset{|}{C}H\cdot CO\cdot C_6H_5 \end{array} + NH_3 = 2H_2O + \begin{array}{l} CH_3\cdot \underset{|}{C}=\overset{|}{C}\cdot C_6H_5 \\ C_6H_5\cdot \underset{|}{C}H\quad \underset{|}{N}H \\ CH_3\cdot \underset{|}{C}=\overset{|}{C}\cdot C_6H_5 \end{array}$$

Action of Ammonia on Phenyldimethyldibenzoylpropane, m. p. 162—163°.—One gram of the compound (m. p. 162—163°) and 5 c.c. of a saturated alcoholic solution of ammonia were heated in a sealed tube to 200° for 8 hours. Upon opening the tube, in which there was scarcely any pressure, an oil remained. The contents of the tube were dissolved in alcohol and allowed to evaporate in a vacuum over sulphuric acid. A small quantity of a pink compound melting at 155—156° was obtained, along with a large quantity of resinous matter. After numerous recrystallisations from alcohol, the former was obtained in colourless needles melting at 155—156°, and was analysed, with the following results:

0·2147 gave 8 c.c. nitrogen at 15° and 759 mm. N = 4·35.

$C_{25}H_{23}N$ requires N = 4·16 per cent.

$C_{25}H_{21}N$ „ N = 4·18 „

From the nitrogen found, this compound may be triphenyldimethyldihydropyridine, $C_{25}H_{23}N$, or triphenyldimethylpyridine, $C_{25}H_{21}N$.

Considering the large amount of resin formed, it is possible that the same changes have gone on as were observed by Michael (*Ber.*, 1885, **18**, 2021) in the formation of $\alpha\gamma$-lutidine-β-carboxylic ester from acetoacetic ester, acetaldehyde, and aldehydeammonia. A similar case was observed by Knoevenagel and Weissgerber (*Ber.*, 1893, **26**, 436) in the formation of pentaphenylpyridine from benzamarone and ammonia. There is, therefore, not merely a separation of water to form a hydropyridine derivative, but possibly a simultaneous oxidation of the hydropyridine ring with formation of 2 : 4 : 6-triphenyl-3 : 5-dimethylpyridine.

This assumption is justified by the fact that the same compound is obtained by the action of hydroxylamine hydrochloride.

Action of Hydroxylamine Hydrochloride on Phenyldimethyldibenzoylpropane (m. p. 162—163°).—Two grams of the substance (m. p. 162—163°), 1 gram of hydroxylamine hydrochloride, and 40 c.c. of 90 per cent. alcohol were heated in a sealed tube at 120—130° for 6 hours. The contents of the tube were precipitated with water and extracted with ether. The ethereal solution left, on evaporation, a pink, crystalline mass, which, after many recrystallisations from alcohol, separated in colourless needles melting at 155—156°. The yield was 70 per cent. of the theoretical. On analysis:

0·2017 gave 0·6622 CO_2 and 0·118 H_2O. C = 89·52; H = 6·49.

0·2012 „ 0·66 CO_2 „ 0·116 H_2O. C = 89·44; H = 6·40.

0·223 „ 8·6 c.c. nitrogen at 13° and 744 mm. N = 4·52.

$C_{25}H_{23}N$ requires C = 89·02; H = 6·82; N = 4·16 per cent.

$C_{25}H_{21}N$ „ C = 89·55; H = 6·27; N = 4·18 „

From the analyses, it is obvious that the compound has the formula $C_{25}H_{21}N$, hence hydroxylamine reacts smoothly with formation of 2 : 4 : 6-triphenyl-3 : 5-dimethylpyridine, thus:

$$\begin{array}{l} CH_3\cdot CH\cdot CO\cdot C_6H_5 \\ C_6H_5\cdot CH \\ CH_3\cdot CH\cdot CO\cdot C_6H_5 \end{array} + OH\cdot NH_2 = 3H_2O + \begin{array}{l} CH_3\cdot C{=}C\cdot C_6H_5 \\ C_6H_5\cdot C \quad N \\ CH_3\cdot C{-}C\cdot C_6H_5 \end{array}.$$

Action of Hydroxylamine Hydrochloride on Phenyldimethyldibenzoylpropane (m. p. 121—122°).—The isomeride (m. p. 121—122°) was not treated with ammonia on account of the very limited quantity obtainable.

0·4 gram of the substance, 0·5 gram of hydroxylamine hydrochloride, and 10 c.c. of 90 per cent. alcohol were heated in a sealed tube at 120—130° for 4 hours, and the product precipitated with water and extracted with ether. Upon evaporation, the ethereal solution deposited a residue of pink crystals, which, after many recrystallisations, were obtained as colourless needles melting at 155—156°. On analysis:

0·18 gave 6·8 c.c. nitrogen at 15° and 752 mm. N = 4·37.

$C_{25}H_{21}N$ requires N = 4·18 per cent.

This compound is identical in appearance and properties with that obtained from the isomeride melting at 162—163° by means of ammonia and of hydroxylamine. The two substances have, therefore, the same structure, and are 1 : 5-diketones of the formula

$$\begin{array}{l} CH_3\cdot CH\cdot CO\cdot C_6H_5 \\ C_6H_5\cdot CH \\ CH_3\cdot CH\cdot CO\cdot C_6H_5 \end{array},$$

but their isomerism is to be explained upon stereochemical grounds.

It is hoped that the substances mentioned in this paper will form the subject of a future communication.

The author wishes to express his indebtedness to Prof. J. Wislicenus for suggesting the above investigation, and for the privilege of being allowed to pursue it in his laboratory.

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XCIX.—*The Decomposition of Chlorates. Part IV. The Supposed Mechanical Facilitation of the Decomposition of Potassium Chlorate.*

By William H. Sodeau, B.Sc.

Very many substances are known to facilitate the decomposition of potassium chlorate, and it has from time to time been suggested that the whole or part of their action is analogous to that of sand, &c., in

promoting the boiling of water. The supposed analogy would, however, appear to be false, it having been shown that the ease of decomposition is not appreciably altered by reducing the pressure to 1 mm. (Trans., 1900, 77, 144). It is difficult to understand why an irreversible decomposition should be facilitated by the presence of solid particles if these are chemically inert. Were the action purely mechanical, it would presumably be common to all finely divided substances, irrespective of their chemical nature, but several workers have stated that zinc oxide, magnesia, &c., produce no facilitation.

There would seem to be a possibility of chemical action in the case of all substances known to facilitate decomposition of the chlorate. For example, the oxides of manganese, iron, cobalt, nickel, and copper cause the oxygen to be very readily evolved, but in each case the existence of an unstable higher oxide is known or indicated. Platinum black is said to have some facilitating action, not, however, comparable with that of the oxides of manganese, &c., but at the temperatures at which this occurs its chemical activity towards oxygen would appear to be considerable. Mond, Ramsay, and Shields (*Phil. Trans.*, 1895, [A], 186, 689; 1897, 190, 153) have shown that after heating at 444° in an atmosphere of oxygen, platinum black contains about 66 times its volume of that gas, and that under similar conditions platinous oxide retains more than a quarter of its oxygen even after many hours' heating. As reduction of pressure was found to diminish these proportions, it would seem that the formation and decomposition of an oxide were probably proceeding simultaneously, hence platinum black cannot well be regarded as chemically inert. References to sand, &c., are discordant, possibly owing to variability of composition.

Veley (*Phil. Trans.*, 1888, [A], 179, 270) maintains that "finely divided chemically inert particles" produce acceleration of the decomposition of potassium chlorate, but publishes only one experiment to establish this, and cites no evidence in support of his assumption that the added substance (barium sulphate) was chemically inert.

The table referring to this experiment appears to indicate that the presence of 1 per cent. of barium sulphate increases the rate of decomposition to the average extent of 500 per cent., but a statement in the text * shows that before systematic observations were taken the average increase amounted only to about 100 per cent. Veley also shows that a similar proportion of manganese peroxide produces a far greater effect.

In the series of experiments described in the present paper (see Table, p. 942), both range and rate of decomposition, and therefore the range of temperature, have been varied in either direction, as com-

* "104 c.c. of gas were given off from the chlorate containing the barium sulphate, but only 51·2 c.c. from that without the sulphate."

pared with Veley's experiment, but the average increase of rate for the presence of 1 per cent. of barium sulphate amounts to only 16 per cent. This is practically negligible, compared with the influence of many other substances, and seems fully explicable by the fact that double decomposition takes place (p. 943) with formation of a small amount of barium chlorate, a substance less stable than potassium chlorate. With 1 per cent. of barium sulphate, the decomposition is very slow at 450°, whilst with 1 per cent. of the peroxide of manganese which is precipitated from the acetate by bromine, the action becomes violent at about 340°.

The author is of opinion that the supposed ability of chemically inert solid particles to facilitate the decomposition of potassium chlorate is unsupported by experimental evidence, and, if existing, is inadequate to explain even a small fraction of the great facilitation produced by the oxides of manganese, iron, cobalt, nickel, and copper. The action of the latter substances, now engaging his attention, would therefore appear to be entirely chemical.

Experimental.

Two specimens of barium sulphate were prepared by precipitating solutions of recrystallised barium chloride with excess of "pure" sulphuric acid, the products being very thoroughly washed by decantation, and dried under reduced pressure. A temperature of 200° was employed in drying the first specimen, but that used in experiment 152 was not previously heated above 100°.

Equal weights of carefully recrystallised potassium chlorate, with and without the addition of 1 per cent. of barium sulphate, were decomposed in similar receptacles placed side by side in a bath of melted pewter, together with a thermometer. The evolved oxygen was collected over water in graduated tubes, readings being taken at intervals of 2 to 10 minutes, and the loss of weight was determined at the conclusion, in order to guard against the possibility of a leak.

The table summarises the results of all such experiments, together with those of the experiment recorded by Veley (*loc. cit.*) ; the numbers given in the latter case were calculated on the assumption that he measured the gas at about 20° and 760 mm., but the main issue would not be affected even if the actual temperature and pressure were widely different from these. All numbers were calculated directly from the gas volumes, and the heating was always continuous, although the earlier and later stages are in most cases given separately.

The weight of each portion of chlorate was 1 gram in experiment 143, 10 grams in experiment 144, and 5 grams in each of the subsequent experiments. Tubes closed at one end were used in

Barium sulphate with potassium chlorate.

Experiment.	$KClO_3$ alone.		$KClO_3$ and 1 per cent. of $BaSO_4$.		Ratio of rates. Mixture / $KClO_3$.
	Range of decomposition (total O = 100).	Percentage of total O per minute.	Range of decomposition (total O = 100).	Percentage of total O per minute.	
143	0—20·3	0·58	0—25·1	0·72	1·23
	20·3 —61·1	0·66	25·1 —62·0	0·61	0·92
144	0— 3·44	0·041	0— 4·08	0·049	1·18
	3·44— 9·6	0·034	4·08—10·6	0·036	1·05
147	0— 1·39	0·0084	0— 5·56	0·034	(4·00)
	1·39— 4·24	0·030	5·56—14·5	0·094	(3·19)
148	0— 1·07	0·0071	0— 1·47	0·0098	1·38
	1·07— 5·94	0·0325	1·47— 8·21	0·045	1·38
149	0— 3·66	0·0152	0— 4·20	0·0175	1·15
150	0— 3·37	0·0087	0— 3·27	0·0085	0·97
			0— 2·54	0·0066	0·75
151	0— 0·35	0·0024	0— 0·54	0·0037	1·5
	0·35— 4·33	0·0306	0·54— 4·46	0·0301	0·98
152	0— 0·34	0·0024	0— 0·40	0·0028	1·19
	0·34— 2·06	0·0107	0·40— 2·42	0·0126	1·17
	0— 0·32	0·0023	0— 0·45	0·0032	1·40
	0·32— 2·13	0·0113	0·45— 2·58	0·0133	1·18
Veley's (*loc. cit.*)	0— 0·25	?	0— 0·51	?	2·03
	0·25— 0·41	0·0019	0·51— 1·48	0·0116	6·06

experiment 143, but submerged bulbs were employed in the other experiments; continual interchange must have eliminated from the average any possible difference due to individual bulb tubes, or to position in the bath.*

Two bulbs containing the mixture were employed in experiment 150; both chlorate and mixture were duplicated in experiment 152.

In some experiments, potassium chlorate mixed with 5 per cent. of potassium sulphate was placed in an additional bulb tube; the potassium sulphate did not appear to have much influence upon the rate of decomposition, but this proportion dissolves in the fused chlorate.

In experiment 147, the behaviour of the pure chlorate was normal, as was shown by the readings of the thermometer and of the volumes of gas evolved from a comparison mixture of chlorate and sulphate of potassium (5 per cent.), but the portion of chlorate mixed with 1

* Veley employed two retorts, each containing 70 grams of potassium chlorate, "placed side by side in a small square air-bath" which was "packed with asbestos, to distribute the heat of the lamp as uniformly as possible."

per cent. of barium sulphate gave results at variance with every other experiment. It seems practically certain that a trace of some impurity must have been introduced, for the subsequent experiments would appear to have excluded every other explanation; experiment 148 was all but identical as regards known conditions, yet it exhibited no such abnormality.

Omitting experiment 147, the average increase of rate for the presence of 1 per cent. of barium sulphate amounted to 16 per cent. (ratio of rates = 1 : 1·16), a result entirely at variance with that obtained by Veley.

Barium sulphate was found to completely dissolve in 500 times its weight of fused potassium chlorate contained in a test-tube placed in a bath of fused potassium nitrate at about 480°, and the "solution" gave a thick precipitate on adding fused potassium chlorate containing potassium sulphate. It is evident that (as on adding barium chloride, Trans., 1900, 77, 146) double decomposition takes place, and that in the present instance barium chlorate and potassium sulphate must be formed. The latter substance does not retard the decomposition of potassium chlorate, consequently the production of barium chlorate, a substance less stable than potassium chlorate, would seem to fully account for the trifling facilitation produced by barium sulphate. When 1 per cent. of barium sulphate is added, the amount rapidly transformed into chlorate must be about a fifth of the whole.

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C.—*The Nutrition of Yeast. Part III.*

By Arthur L. Stern, D.Sc.

The work described in the two preceding parts (Trans., 1899, 75, 202; *J. Fed. Inst. Brewing*, 1899, 399) was continued with the object of obtaining a knowledge of the effect which conditions other than those already discussed had on the growth of yeast, its composition, and the relations of these to the progress of the fermentation.

The experimental method has already been described in Part I; briefly, it is as follows. Into a flask holding rather more than a litre are introduced 500 c.c. of a solution of dextrose (*d*-glucose) of definite strength, 1·5 grams of crystallised asparagine, 0·5 gram of potassium phosphate, 0·2 gram of magnesium sulphate, and 0·02 gram of calcium sulphate. The neck of the flask is closed with a cotton wool plug, and the contents are boiled for 10 minutes. When cool, the yeast is added.

This was obtained in the manner described in Part I from the same culture of Burton yeast then prepared.

The sugar solution when thus seeded was kept at a constant temperature until the conclusion of the experiment. The yeast was then removed by filtration, dried at 100° until constant, and the nitrogen contained in it estimated. The optical activity of the fermented solution indicated the amount of sugar remaining unfermented.

No difficulty was experienced in filtering off the yeast, except when the fermentation was still proceeding. In these experiments, the addition of 0·5 gram of salicylic acid dissolved in 10 c.c. of alcohol to the 500 c.c. of fermenting solution at once stopped the fermentation, and the yeast could be easily removed.

(1) *The Influence of Concentration.*—J. Archleb (*Zeit. Spiritusind.*, 11, 243), using maltose solutions varying in concentration between 1 and 25 per cent., found that as the concentration of the sugar was increased, (*a*) from 1 to 5 per cent., the weight of yeast obtained increased; (*b*) from 5 to 10 per cent., the weight of yeast crop increased but slightly; (*c*) from 10 to 14 per cent., the weight of yeast crop increased rapidly; (*d*) from 14 to 19 per cent., the weight of the yeast crop diminished; (*e*) from 19 to 25 per cent., the weight of the yeast crop again increased. These experiments indicate that the weight of the yeast crop varies irregularly as the concentration of the sugar is increased.

Experiments were made according to the method described above to obtain further information on this point. They were performed at 25°, and the amount of seeding was 1·5 cells per 1/4000 cub. mm.

The results are given in Tables 1*a* and 1*b* (p. 945). The only difference in the conditions of the two series of experiments is that those of Table 1*b* were performed with 0·75 gram of asparagine per 500 c.c. of solution instead of 1·5 grams used in all the other experiments.

As the standard time of fermentation (7 days) allowed in the earlier experiments was found to be insufficient when fermenting solutions containing more than 15 per cent. of dextrose, experiments with these solutions were repeated, allowing a longer time for fermentation.

Curve 1 (p. 946) was drawn by joining the points obtained by taking as abscissæ the weights of nitrogen contained in the yeast, and as ordinates the concentration of the sugar at the commencement of the fermentation; it clearly shows that as the concentration rises from zero the amount of nitrogen assimilated increases rapidly at first, then more slowly, until with concentrations of more than 15 per cent. the increase appears almost to cease; there is, however, much difficulty in completing the fermentation with concentrations exceeding 20 per cent.

The percentage of nitrogen in the yeast does not greatly vary, but is highest with the weakest and strongest solutions here employed.

TABLE 1*a*.

Duration of fermentation.	Percentage of dextrose before fermentation.	Weight of nitrogen in yeast crop. Gram per 100 c.c.	Percentage of nitrogen in yeast crop.	Percentage of dextrose unfermented.	Weight of yeast crop. Gram per 100 c.c.
7 days	0	0·0028	7·0	—	0·040
,,	1	0·0081	8·6	0	0·094
,,	3	0·0129	7·8	1·5	0·166
,,	5	0·0178	7·9	2·8	0·226
,,	7·5	0·0200	7·1	3·1	0·280
,,	10	0·0216	6·9	4·2	0·314
,,	12·5	0·0246	7·0	6·0	0·352
,,	15	0·0275	7·2	6·6	0·382
,,	20	0·0167	6·7	37·4	0·248
,,	25	0·0148	7·0	51·5	0·211
,,	30	0·0122	7·7	65·2	0·160
10 days	12·5	0·0230	7·4	5·3	0·311
,,	15·0	0·0238	7·3	5·1	0·326
,,	17·5	0·0232	7·6	5·4	0·306
,,	20·0	0·0252	7·8	6·6	0·322
,,	22·5	0·0253	7·9	10·5	0·320

TABLE 1*b*.

Duration of fermentation.	Percentage of dextrose before fermentation.	Weight of nitrogen in yeast. Gram per 100 c.c.	Percentage of nitrogen in yeast.	Percentage of sugar unfermented.	Weight of yeast. Gram per 100 c.c.
7 days	0	0·0028	7·0	—	0·040
,,	1	0·0076	9·0	4·7	0·085
,,	3	0·0122	7·4	1·8	0·165
,,	5	0·0165	7·4	1·9	0·221
,,	7·5	0·0194	6·6	2·2	0·293
,,	10	0·0212	6·6	5·8	0·323
,,	12·5	0·0236	6·6	5·0	0·361
,,	15	0·0199	6·8	12·6	0·291
,,	20	0·0190	6·5	34·5	0·293
,,	25	0·0160	7·1	50·4	0·224
,,	30	0·0129	7·4	62 0	0·175

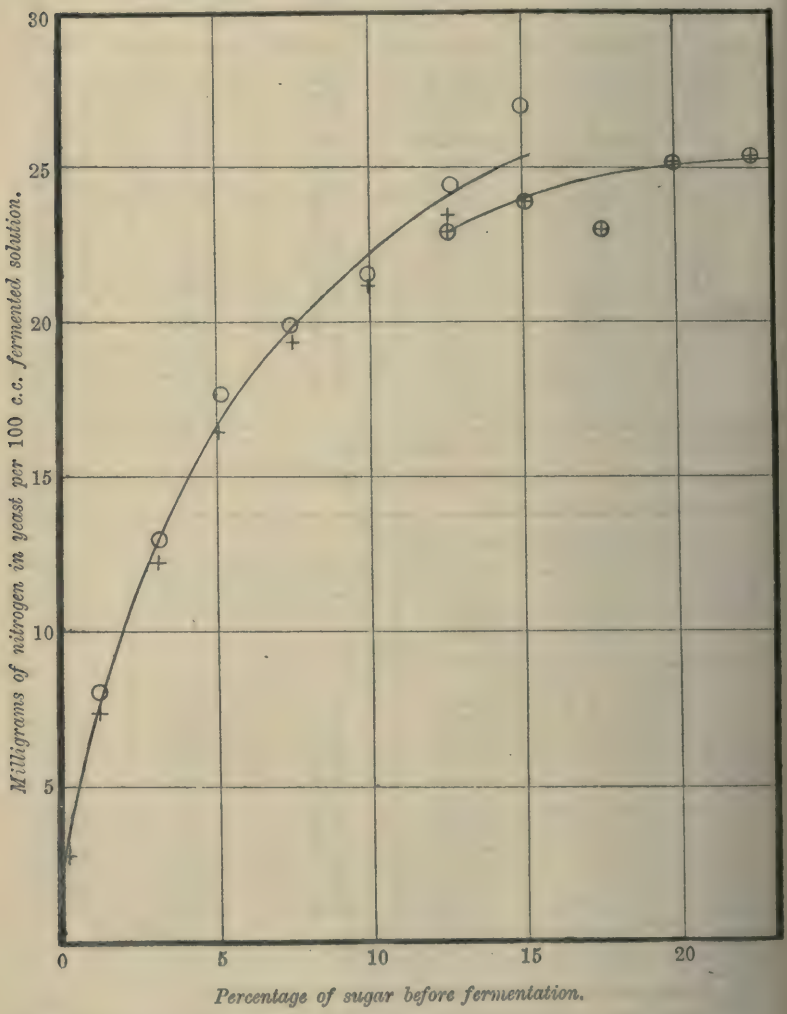
No yeast growth was obtained when no sugar was present.

(2.) *Influence of Temperature.*—R. Pedersen (*Carlsberg Lab. Reports*, 1878, 22) found that the yeast cells increase in number most rapidly at 28°, but that the same total number was produced at 13·5° as at 23°, and that no growth took place at 38°.

The experiments summarised in Table 2 were all carried out with

10 per cent. dextrose solutions, and the inorganic and nitrogenous nutriment stated above at the temperatures noted. The amount of seed yeast was the same as before. In order that the fermentations

CURVE 1 (TABLE 1).



could be completed, the time of fermentation had to be considerably longer at the lower temperatures.

These results indicate that at temperatures between 12° and 25° there is little difference in the weight of yeast, and the amount of

nitrogen contained by it, but that at 30° and above there is a decrease of these factors, and at 37° it is evident that the functions of the yeast are seriously weakened.

TABLE 2.

Temperature.	Duration of fermentation.	Weight of nitrogen in yeast crop. Gram per 100 c.c.	Percentage of nitrogen in yeast crop.	Percentage of sugar unfermented.	Weight of yeast crop. Gram per 100 c.c.
12°	13 days	0·0194	7·7	14·7	0·252
15·5	16 ,,	0·0198	6·8	3·6	0·291
18	12 ,,	0·0221	6·6	4·7	0·337
21	9 ,,	0·0224	6·6	9·2	0·339
25	7 ,,	0·0212	6·9	4·4	0·310
30	5 ,,	0·0173	7·2	5·6	0·243
37	3 ,,	0·0085	7·8	40·1*	0·110

* Six days' fermentation produced but a slight increase in the amount of sugar fermented and a decrease in the weight of yeast.

(3.) *The Effect of Varying the Amount of Seed Yeast.*—A. J. Brown (Trans., 1892, 61, 369) has shown that for any one fermentable solution there is a constant number of yeast cells up to which the yeast will increase if the solution be seeded with a smaller number, and that if it be seeded with a larger number no increase in the number of cells will take place.

The experiments summarised in Table 3 were made more particularly to ascertain the relationship between the weight of nitrogen contained in the seed yeast and that contained in the final yeast crop at the conclusion of the fermentation. They were carried out at 25° with the quantities of nitrogenous and inorganic nutriment given above, but in view of the great importance of the results three series of experiments were made with 5, 10, and 15 per cent. dextrose solutions.

On comparing the figures obtained by subtracting the weight of nitrogen added in the seed yeast from that contained in the yeast crop, it is found (except where the seeding is less than 5 per cent. of the crop) that within the limits of experimental error the figures are the same for any one solution, and that, as might be expected from the previous experiments on the effect of concentration, the average for the 5 per cent. solutions is the least, and that for the 15 per cent. solution the greatest. In the experiments where the seeding was less than 5 per cent. of the crop, these differences are below the average.

As the percentage of nitrogen contained in the yeast does not vary very materially, these results may be taken as also applying to the

TABLE 3.

Weight of nitrogen in the		Difference between the values in the first two columns.	Percentage of nitrogen in the yeast.	Percentage of sugar unfermented.
Yeast crop. Gram per 100 c.c.	Seed yeast. Gram per 100 c.c.			
(*a*) Five per cent. sugar solutions:				
0·0121	0·0005	0·0116	6·8	2·8
0·0144	0·0006	0·0138	7·1	1·9
0·0151	0·0014	0·0137	6·7	1·1
0·0167	0·0019	0·0148	7·4	1·9
0·0176	0·0040	0·0136	7·3	2·8
0·0179	0·0056	0·0123	7·3	2·8
0·0236	0·0112	0·0124	7·7	3·4
	Mean.....	0·0132		
(*b*) Ten per cent. sugar solutions:				
0·0143	0·0002	0·0141	6·9	3·0
0·0155	0·0006	0·0149	7·0	2·0
0·0161	0·0008	0·0153	6·8	11·3
0·0196	0·0017	0·0179	7·1	5·1
0·0204	0·0023	0 0181	6·6	6·2
0·0218	0·0045	0·0173	6·5	2·8
0·0217	0 0050	0·0167	7·1	3·0
0·0247	0·0066	0·0181	6·5	3·3
0·0269	0·0096	0·0173	7·0	3·0
0·0308	0·0125	0·0183	6·6	2·3
0·0352	0·0172	0·0180	7·1	3·0
	Mean.....	0·0177*		
(*c*) Fifteen per cent. solutions:				
0·0173	0·0009	0·0164	7·1	5·0
0·0201	0·0013	0·0188	6·3	9·5
0·0214	0·0027	0·0187	7·0	3·9
0·0248	0·0040	0·0208	6·1	6·3
0·0228	0·0072	0·0156	6·7	4·6
0·0318	0·0135	0·0183	6·6	3·9
	Mean.....	0·0181		

* Mean of the last eight values.

weight of the yeast, and except when the seeding is very small, a general statement of the result may be made as follows. If to equal

volumes of any one fermentable solution quantities of yeast a, b, c be added, the resultant crop of yeast at the end of the fermentation will be $a+p$, $b+p$, $c+p$, where p is a constant quantity dependent on the composition of the solution.

If the seeding is very large, this statement must be modified, as yeast always contains some dead or weak cells, and the decomposition of these would introduce more yeast nutriment into the solution.

(4) *Effect of Time.*—It is generally stated that most of the yeast is formed during the early stages of the fermentation and that in the later stages there is little, if any, increase of yeast (Mohr, *Wochenschr. Brau.*, 1896, **3**, 210; F. Schonfeld, *ibid.*, 421; Delbruck, *Bied. Centr.*, 1880, 217; Boulanger, *Ann. Inst. Pasteur*, 1896, **10**, 598).

To determine the relation of the weight and nitrogen contents of the yeast to the amount of sugar fermented at successive time intervals, experiments were performed at 25° with 10 per cent. dextrose solutions, and the amounts of nitrogenous and inorganic nutriment already noted; the results are given in Table 4 (p. 950). The amount of seed yeast in the four series of experiments a, b, c, and d was in the proportions of 1, 3, 9, and 14.

Curve 2 (p. 951) was drawn by joining the points obtained by taking as abscissæ the weight of nitrogen in the yeast, and as ordinates the corresponding amount of sugar fermented. It clearly shows that the increase of the yeast, and of the weight of nitrogen contained in it, goes on to the end of the fermentation.

After a certain time, which is least in series c, the curve becomes a straight line; that is, the ratio of the amount of sugar fermented to the weight of nitrogen remains constant during the remainder of the fermentation. The curves show that before constancy is reached, the nitrogen increases more rapidly than the amount of sugar fermented, when the seeding is less than in c (compare a and b), and less rapidly when it is greater than in c (compare d).

As the percentage of nitrogen in the yeast does not vary much throughout the fermentation, these statements are practically also true for the ratio of the weight of yeast to the weight of sugar fermented.

The experiments described in this investigation were primarily made with the object of obtaining a knowledge of the effect of different conditions on the growth of the yeast and its composition, and the relation of these to the progress of the fermentation.

As it was necessary to work under conditions which could at any time be exactly reproduced, the choice of yeast foods was restricted to such as could be obtained pure in reasonable quantity. It is known that when employing such yeast foods as are contained in malt worts, yeast water, &c., larger and more nitrogenous yeast crops are obtained. It is thus possible that the results here obtained may be in some

respects abnormal. The author hopes to investigate this question in the future.

TABLE 4.

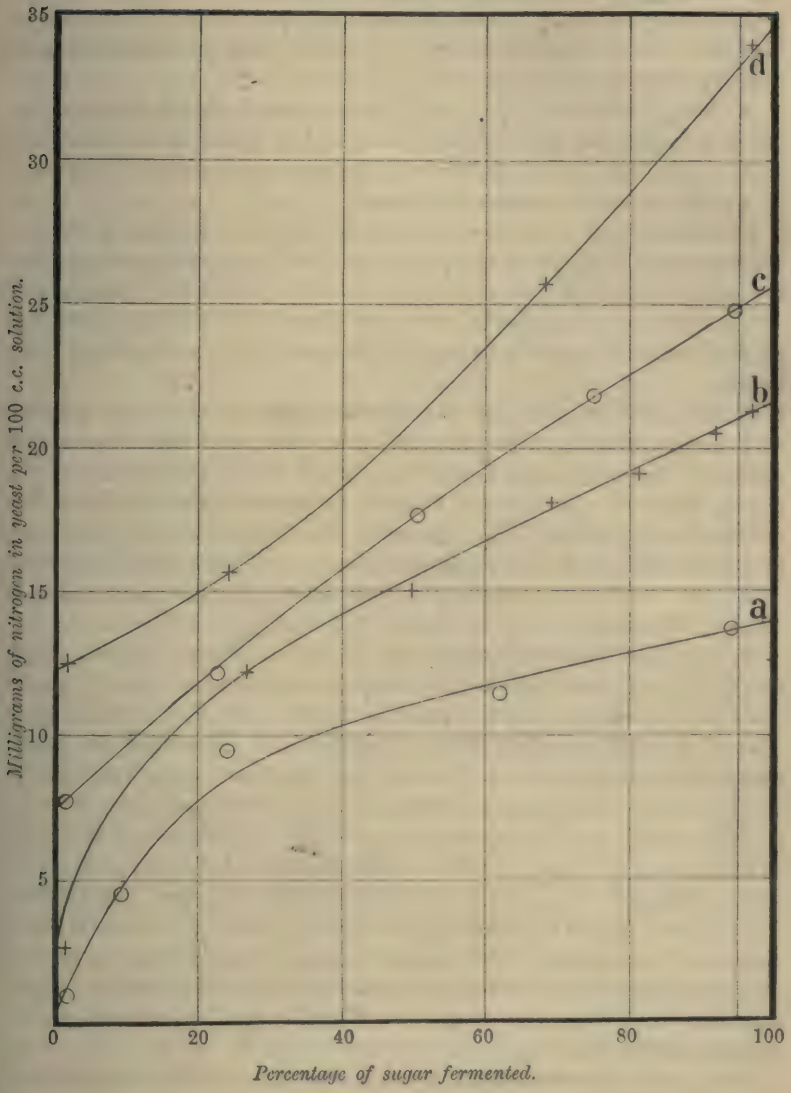
Time.	Weight of nitrogen in yeast. Gram per 100 c.c.	Percentage of nitrogen in yeast.	Percentage of sugar unfermented.	Weight of yeast. Gram per 100 c.c.
Series *a*:				
0	0·0009	7·5	100·0	0·012
2 days	0·0045	7·2	90·9	0·065
4 ,,	0·0095	6·5	66·0	0·147
6 ,,	0·0116	6·0	38·9	0·193
10 ,,	0·0138	6·2	6·0	0·223
Series *b*:				
0	0·0026	7·0	100.0	0·037
1 day	0·0120	8·0	75·6	0·161
2 ,,	0·0150	7·0	50·8	0·217
3 ,,	0·0180	7·0	30·8	0·260
4 ,,	0·0191	6·9	18·6	0·279
5 ,,	0·0205	6·9	8·4	0·296
7 ,,	0·0212	6·9	4·4	0·310
Series *c*:				
0	0·0078	7·1	100·0	0·110
1 day	0·0123	6·6	77·6	0·185
2 ,,	0·0178	6·1	49·3	0·290
3 ,,	0·0220	6·1	25·1	0·364
5 ,,	0·0249	6·1	5·4	0·406
Series *d*:				
0	0·0125	6·1	100·0	0·206
14 hours	0·0157	6·8	75·6	0·229
38 ,,	0·0259	6·2	32·0	0·419
86 ,,	0·0340	6·2	3·5	0·548

The results here obtained may be summarised as follows:

1. Any increase of nitrogenous or inorganic nutriment beyond a definite limit will not increase either the amount of nitrogen assimilated by the yeast or the weight of the yeast. This limit is but little greater than the largest amount which the yeast is able to assimilate under the conditions of the experiment (Part I, *loc. cit.*).

2. An increase of the sugar is accompanied by an increase in the weight of nitrogen assimilated and in the weight of the yeast. This increase continues up to the strongest concentrations which can be completely fermented. The *rate* of increase is greatest at the lowest concentrations and falls off gradually as the concentration rises.

CURVE 2 (TABLE 4).



3. Temperatures between 12° and 25° have but little influence on the weight of nitrogen assimilated and the weight of the yeast crop. At higher temperatures, reproduction is weakened.

4. The total weight and nitrogen content of the yeast crop obtained at the completion of fermentation are dependent solely on the weight

and nitrogen content of the yeast added to produce fermentation and on the composition of the fermentable solution.

5. During a portion of the fermentation the growth of yeast is proportional to the amount of sugar fermented, and proceeds as long as any sugar remains unfermented.

Although the chief object of this work was to obtain these results, yet it was thought that when obtained they would throw additional light on the mechanism of fermentation and yeast growth; that they do so will be seen from the following.

Statements 1 and 2 show that there must be a great difference between the functions of the nitrogenous and inorganic nutriment, on the one hand, and of the sugar on the other; whilst the function of the first two is to supply the necessary *material* to form the yeast, that of the sugar is twofold—to supply the yeast with *material* and with *energy*.

The chemical products of the decomposition of the sugar (alcohol and carbon dioxide) are useless to the yeast, and when present in sufficient quantity even deleterious to it; this decomposition of the sugar, however, sets free an amount of energy which has been calculated as from 33 to 67 K; the heat developed has been measured, and amounts to 23·5 K according to Bouffard (*Compt. rend*, 1895, **121**, 357), and to 21·4 K according to A. J. Brown (*J. Fed. Inst. Brewing*, 1901, **7**, 93).

It has been previously suggested by A. J. Brown (Trans., 1894, **59**, 911), by Reynolds Green (*Fermentation*, p. 334), and others that the need for this energy is the reason for the fermentation of the sugar, part of it being employed to carry on the vital actions of the yeast, and part to raise the temperature of the solution, a temperature slightly above the ordinary being most favourable to the yeast.

It is a much debated question whether the fermentation of the sugar is the work of an enzyme or of the vital functions of the yeast. Buchner (*Ber.*, 1897, **30**, 117, 1110, 2668; 1898, **31**, 209, 568, 1084, 1090, 1531; 1899, **32**, 127), Abeles (*Ber.*, 1898, **31**, 2261), and others state that they have isolated this ferment from yeast; this explanation of their experiments has, however, been combated by Macfadyen, Morris, and Rowland (*Proc. Roy. Soc.*, 1900, **67**, 250) and Wróblewski (*Centr. Physiol.*, 1899, 22).

The great difficulty attending the investigation of the fermentative function of yeast has been to eliminate disturbances due to change in the fermentative power of the plant—that is, to change in the amount of fermentative enzyme, supposing such to be present. Dumas (*Ann. Chim. Phys.*, 1874, [v], **3**, 81) and A. J. Brown (Trans., 1892, **61**, 369) employed such an excess of yeast as was shown by the latter to result in fermentation without any numerical increase of yeast, and found

that under these conditions equal quantities of sugar were fermented in equal times. If no change had taken place in the fermentative power of the yeast during the experiment, this result would negative the enzyme theory. It is, however, quite possible that the fermentative power of the yeast has changed in the course of the experiments, and for the following reasons.

It is shown in Table 4 that fermentation is closely connected with yeast growth, and if yeast growth has taken place, the fermentative power of yeast as a whole has probably changed.

Now, in two of A. J. Brown's experiments (*loc. cit.*, 377), in which a large excess of yeast was employed, and no numerical increase took place, the weight of the yeast had appreciably increased during the fermentation.

Moreover, J. O'Sullivan (*J. Fed. Inst. Brewing*, 1899, **5**, 101) showed that whilst the invertive function of living yeast could be and was usually exercised without yeast growth taking place, this was not the case with the fermentative function. Other evidence indicating the intimate connection between yeast growth and fermentation is to be found in the experiments described above (statements 4 and 5) and in the stimulating effect of nutriment in increasing the rapidity of fermentation of a non-multiplying yeast (J. O'Sullivan, *J. Soc. Chem. Ind.*, 1898, **17**, 559).

Even supposing that, by using a large excess of yeast, it were possible to obtain fermentation, without any apparent increase either in the weight of the yeast or in the number of yeast cells, yet it would be quite possible for yeast growth to take place at the expense of the decomposition products of dead cells which are always present, decomposed yeast being an excellent yeast food. If yeast growth has taken place, there will probably be some change in the fermentative power of the yeast as a whole.

The experiments of Dumas and Brown do not then disprove the enzyme theory. There is thus no proof that the fermentation of sugar by yeast is not caused by an enzyme, and whilst the converse has not yet been definitely proved, the evidence at present available points in this direction. The enzyme (if existent) is exceedingly unstable; it diminishes in amount, even in living yeast cells which have remained quiescent for a short time,* but when required by growing yeast it is abundantly secreted. This view derives some support from the fact that the change in the appearance of the yeast cells when sown in a fermentable solution is similar to that which takes place in the columnar cells in the germinating barley embryo when secreting diastase.

* Buchner and Rapp (*Ber.*, 1897, **30**, 2668) state that it can only be prepared from fresh yeast.

CI.—*Oroxylin.*

By William Arthur Harrison Naylor and Charles Stanley Dyer.

The bark of *Oroxylum indicum* was examined by Naylor and Chaplin in 1890 (*Year Book of Pharmacy*), and among the substances then separated was a yellow, crystalline compound, to which they gave, provisionally, the name of oroxylin. Its conduct towards certain reagents was noted, and particularly its behaviour with sodium and potassium hydroxides, which resulted in the production of an intense red colour, quickly passing into a dark green.

For the opportunity to study more intimately this interesting constituent, we are indebted to Mr. David Hooper, of Calcutta, who kindly collected and shipped to one of us a considerable quantity of the bark.

Isolation of Oroxylin.

The bark, reduced to No. 20 powder, was exhausted with 90 per cent. alcohol by percolation, the percolate concentrated by distilling off most of the spirit, and the resulting liquid poured into eight times its volume of water, when the oroxylin was precipitated together with wax, fat, and resinous substances. The bulky precipitate was collected, washed with water, and dried in a water-oven. When quite dry, it was treated with chloroform until most of the wax, fat, and resinous substance had been withdrawn. It was then exhausted with ether, the ethereal liquid distilled, and the residue washed with light petroleum to remove the last traces of fat. This purified residue was dissolved in alcohol, in which it readily dissolved. The solution, after filtration, was diluted with hot water until a faint cloudiness appeared, and set aside to crystallise.

The yield of pure oroxylin is about 2 parts per 1000. It crystallises in sharply defined, golden-yellow needles about 1/6 inch in length, is readily soluble in alcohol or hot glacial acetic acid, less so in ether, sparingly so in chloroform, and practically insoluble in water. Oroxylin begins to melt at 225°.

When burnt with cupric oxide in a current of oxygen, the following numbers were obtained:

	(1).	(2).	(3) Werner.	$C_{19}H_{14}O_6$ requires
C.....	67·42	67·43	67·49	67·45 per cent.
H	4·51	4·6	4·38	4·14 ,,

For the purpose of comparison, we give the percentage numbers obtained by Werner (*Pharm. Journ.*, 1898, [iv], 7, 390), and it will be noted that ours are in close agreement with his. From these figures,

and others to be presently mentioned, we believe the formula for oroxylin to be $C_{19}H_{14}O_6$.

As oroxylin rapidly reduces silver compounds, the formation of a definite silver salt was not possible.

The addition of lead acetate dissolved in weak alcohol to an alcoholic solution of oroxylin gives a light red, bulky precipitate of indefinite composition.

Derivatives of Oroxylin.

Triacetyloroxylin, $C_{19}H_{11}O_6(C_2H_3O_2)_3$.—In our first attempt to acetylate oroxylin we acted on it direct with acetyl chloride, but the method proved unsatisfactory, the product being resinous and the yield of crystallisable substance disproportionately small.

Eventually, the acetic anhydride and dry sodium acetate were adopted. The action which in the early stages took place rapidly, on the application of the heat of a water-bath, was complete in half an hour. On cooling, the whole solidified, forming a crystalline mass.

To isolate the derivative, the mixture, after the addition of a little ether, was poured into water. The ether was blown off, when the insoluble product gradually solidified. It was collected, washed with water, then cautiously with ether which removed resinous matter, and finally was crystallised from alcohol. This colourless product consisted of minute, white, acicular crystals melting at 150—152° with partial decomposition into oroxylin.

When hydrolysed by warming for half an hour with slightly diluted sulphuric or hydrochloric acid and then pouring the liquid into water the regenerated oroxylin is precipitated, and may be collected, washed with water, dried at 110°, and weighed. In this manner, the following results were obtained from the acetyl derivative by hydrolysis:

(i) 0·279 gave 0·205 oroxylin, equivalent to 73·47 per cent.
(ii) 0·302 „ 0·220 „ „ 72·84 „
(iii) 0·430 „ 0·314 „ „ 73·02 „

$C_{19}H_{11}O_6(C_2H_3O)_3$ contains oroxylin = 72·84 per cent.

Dibromoroxylin, $C_{19}H_{12}O_6Br_2$.—One gram of oroxylin was dissolved by heating with 20 c.c. of glacial acetic acid, and to the solution was added 1 c.c. of bromine. The mixture was allowed to evaporate on a water-bath until it commenced to crystallise, when it was set aside and the mother liquor poured off from the crystalline magma. The product, after three recrystallisations from acetic acid, was obtained in pale yellow needles which began to melt at 173° and dissolved readily in alcohol or ether.

0·308 gave 0·233 AgBr. Br = 32·19.
0·428 „ 0·320 AgBr. Br = 31·81.

$C_{19}H_{12}O_6Br_2$ requires Br = 32·23 per cent.

Decomposition Products.

Oroxylin was boiled for half an hour with a 50 per cent. solution of caustic potash. When cold, it was diluted with water, neutralised with hydrochloric acid, and agitated with ether. The ethereal layer yielded a small quantity of a neutral substance, which, after purification, answered the test for phloroglucinol with pinewood and hydrochloric acid. The neutralised liquid was then acidified and again shaken with ether. The ethereal layer left, after evaporation, a much coloured residue. The crude product was extracted with light petroleum, which by slow evaporation gave a crop of fine, colourless needles having an aromatic odour. This crystalline substance sublimed unchanged, melting at 120°. An aqueous solution, when neutralised by caustic soda, gave a reddish-brown colour with neutral ferric chloride. Its melting point, solubilities, and behaviour towards reagents afford conclusive evidence that it is benzoic acid.

A second quantity of oroxylin was similarly treated with a 20 per cent. solution of caustic potash with a similar result, except that in addition to benzoic acid a small quantity of phthalic acid was detected.

A third quantity was digested for half an hour with fused potash maintained at a temperature of about 180°. Again the chief product proved to be benzoic acid.

When oroxylin was allowed to stand in a 5 per cent. solution of potassium hydroxide at the ordinary temperature, a considerable liberation of benzaldehyde occurred.

Potassium permanganate is instantly decolorised by oroxylin, phthalic acid being one of the products of the reaction, as recognised through the fluorescence resulting from the interaction with resorcinol.

The following negative results indicate the absence of a methoxyl or ketonic group in oroxylin, and also prove that it is not a weak acid.

1. The application of Zeisel's method for the estimation of methoxyl gave negative results.

2. When treated with a mixture in suitable proportions of potassium iodide and iodate, there was not the faintest liberation of iodine.

3. Several attempts were made to induce oroxylin to interact with phenylhydrazine, but without success, neither phenylhydrazine in the presence of acetic acid, nor its hydrochloride, with or without acid, sufficed to convert it into a hydrazone.

Summarising the results at present obtained, it appears that oroxylin forms a dibromo-derivative, that it contains an easily detached benzene nucleus, that three hydroxyl groups are present, and that its composition may be represented by the formula $C_{19}H_{14}O_6$.

CII.—*Optically Active Dimethoxysuccinic Acid and its Derivatives.*

By Thomas Purdie, F.R.S., and James C. Irvine, B.Sc.

Previous papers on the use of silver oxide and alkyl iodide in alkylating the esters of hydroxy-acids have shown that optically active mono- and di-alkyloxysuccinic and alkyloxypropionic acids can be readily obtained from active malic, tartaric, and lactic acids by this method.

The alkyloxysuccinic acids mentioned are substances of considerable interest from a stereochemical point of view. Their close relationship to the common hydroxy-acids, which have formed the subject of so much research in this particular field, imparts of itself a special interest to them. Their etheric character protects them from the disturbing effects which the hydroxyl group is known to exercise on optical activity, and unlike most of the acyl derivatives of the hydroxy-acids, they can be examined as free acids or salts in solution without risk of decomposition. They are endowed with much higher optical activity than the parent acids, and are therefore well adapted for the investigation of problems relating to this property. We have already described various representatives of this class of optically active compounds, but it is evident that if general conclusions are to be reached on the points raised by their study, more extensive series of them must be examined.

The present paper deals with dimethoxysuccinic acid, its methyl, ethyl, and propyl esters, and some of its metallic salts.

Methyl d-*Dimethoxysuccinate.*

The observed rotation of the methyl tartrate used in the preparation of this compound was $+2{\cdot}82°$ in the superfused state ($l = 1$, $t = 20°$), the corresponding value recorded by A. Pictet being $2{\cdot}84°$. On adding the silver oxide (3 mols.) to the solution of the tartrate (1 mol.) in methyl iodide (6 mols.), a vigorous action ensued, which had to be moderated by cooling. After heating the mixture for some time on a water-bath, filtering, and distilling off the ether which was used in washing the silver iodide, a liquid was obtained which boiled nearly constantly at 132° under 12 mm. pressure and gave a distillate which crystallised quickly in radiating prisms. The substance, after being recrystallised from ether, melted at 51°, and gave on analysis :

I. C = 46·70 ; H = 7·12. II. C = 46·55 ; H = 6·98.

$C_8H_{14}O_6$ requires C = 46·60 ; H = 6·80 per cent.

The compound is readily soluble in water without undergoing perceptible hydrolysis, also in alcohol, benzene, or chloroform, and may be conveniently crystallised from carbon disulphide or ether. Unlike methyl tartrate, it cannot be kept superfused, and the rotation of the pure liquid had therefore to be taken at 60°. The result was $\alpha = +93{\cdot}48°$, $l = 1{\cdot}001$, $d\ 60°/4° = 1{\cdot}1317$, hence $[\alpha]_D^{60°} = +82{\cdot}52°$.

In preparing ethyl diethoxysuccinate from ethyl tartrate (*loc. cit.*), the crude product contains a considerable quantity of a less active compound, which is removed with some difficulty. The reaction between methyl tartrate and methyl iodide, on the other hand, gives an almost quantitative yield of dimethoxysuccinate; from 45 grams tartrate we obtained 46 grams of the recrystallised substance. The fact that three different preparations showed practically the same specific rotation, namely, +104·66°, 104·47°, and 104·60° in a 10 per cent. benzene solution at 20°, indicates that racemisation does not occur in the course of the chemical action, and this was further confirmed by finding that fractional crystallisation produced no appreciable change of activity.

Ethyl d-*Dimethoxysuccinate.*

In preparing the alkyloxypropionic esters containing two different alkyl groups (Trans., 1899, **75**, 486), it was found that the hydroxyl of the ethereal lactates can be alkylated with silver oxide and alkyl iodide without any interchange with the carboxylic alkyl group occurring. We find that tartaric esters behave similarly, ethyl dimethoxysuccinate being produced by the action of methyl iodide and silver oxide on ethyl tartrate.

The ethyl tartrate used in our preparations gave $\alpha = +9{\cdot}11°$ ($l = 1$, $t = 20°$), Pictet's value being 9·24°. The proportion of materials and the method of procedure were the same as described above; the reaction here was apparently less vigorous, and a perceptible quantity of water was produced. From 41 grams of ethyl tartrate we obtained 42·5 grams of a thick, yellowish oil, which boiled at a nearly constant temperature, and gave the rotation $\alpha^{20°} = 95{\cdot}96°$ ($l = 1$). The methods used in the case of the methyl ester, for assuring ourselves that the action was complete, not being available, the product was subjected to further treatment with silver oxide and methyl iodide. A second treatment with a third of the quantities of the reagents originally used raised the rotation to 98·66°; after a third similar treatment, the rotation found was 98·47°, and after another distillation (b. p. 155° under 25 mm. pressure) 98·61°. The substance was accordingly regarded as pure.

Analysis gave:

C = 51·33; H = 7·82. $C_{10}H_{18}O_6$ requires C = 51·28; H = 7·69 per cent.

The compound was further identified by analysis of the dried barium salt obtained from it by hydrolysis with barium hydroxide, which gave Ba = 43·91, the calculated number for barium dimethoxysuccinate being 43·77, and by the fact that the acid prepared from this barium salt possessed the same activity as that prepared from methyl tartrate in the reaction already described.

The ester did not solidify, and was much less soluble in water than the methyl homologue. Specific rotations taken in a 1 dcm. tube gave :

$d\ 10°/4° = 1·1055$, $[\alpha]_D^{10°} = +90·70°$.
$d\ 15°/4° = 1·1020$, $[\alpha]_D^{15°} = 90·26$.
$d\ 20°/4° = 1·0961$, $[\alpha]_D^{20°} = 89·96$.
$d\ 60°/4° = 1·0556$, $[\alpha]_D^{60°} = 85·39$.

Propyl d-*Dimethoxysuccinate.*

We are indebted to Mr. E. J. Balfour, who is preparing some of the higher dialkyloxysuccinic esters, for the following data concerning this compound :

$\alpha^{20°} = +90·12°$, $l = 1$, $d\ 20°/4° = 1·0612$, $[\alpha]_D^{20°} = +84·92°$.
$\alpha^{60°} = +82·98°$, $l = 1$, $d\ 60°/4° = 1·0237$, $[\alpha]_D^{60°} = +81·06°$.

d-*Dimethoxysuccinic Acid.*

This acid was prepared from the methyl ester by hydrolysing it with a 10 per cent. aqueous solution of potassium hydroxide, acidifying, and extracting with ether, and also from the methyl and the ethyl esters by hydrolysing with barium hydroxide and decomposing the crystallised hydrated barium salt with the calculated quantity of sulphuric acid. The latter is the preferable method, as ether does not extract the acid easily from an aqueous solution. The compound is readily soluble in water, alcohol, or acetone, much less so in ether, and is scarcely dissolved by benzene or carbon disulphide. It crystallises from water in small prisms and from acetone in large plates. Crystals obtained from an aqueous solution, after drying in a vacuum, melted at 151°, but not very sharply, owing perhaps to slight decomposition.

Analysis of the acid, dried at 100°, gave

C = 40·26 ; H = 5·77.

$C_6H_{10}O_6$ requires C = 40·45 ; H = 5·62 per cent.

Observations on the rotatory power of the acid in solution are recorded below.

The diacyl- and dialkyl-succinic acids in general yield anhydrides readily, and the dialkyloxysuccinic acids might be expected to behave similarly. Our attempts, however, to prepare dimethoxysuccinic

anhydride were not successful. When the dry acid was treated with boiling acetyl chloride, and the excess of the reagent then evaporated, the residual liquid deposited well formed cubes, which melted at a much lower temperature than the acid, namely, at about 77°, and the substance still retained the low melting point after recrystallisation from chloroform. On recrystallising, however, from boiling ether, needles were obtained which had approximately the same melting point as the acid. The melting point rose in a similar manner on heating the substance at 100°, and on letting it stand for some days at the ordinary temperature in a vacuum. The low melting point might perhaps be due simply to solvent adhering to the acid, and the subsequent rise to its removal, but the observations suggest the possibility of isomeric change, and we intend to examine the reaction with larger quantities of material. An attempt to convert the acid into anhydride by distilling in a vacuum resulted in complete decomposition.

d-*Dimethoxysuccinamide.*

When a concentrated solution of the methyl ester in methyl alcohol was saturated with ammonia, this compound was deposited slowly in the form of a mass of felted needles. After being dried at 100°, it was analysed with the following results:

I. C = 40·86; H = 7·22. II. C = 40·84; H = 7·10; N = 16·09.
$C_6H_{12}O_4N_2$ requires C = 40·91; H = 6·82; N = 15·91 per cent.

The substance is insoluble in the ordinary organic solvents, and very sparingly soluble in cold water, but more soluble in boiling water, from which it crystallises unchanged. As the following observations of its optical activity had consequently to be made on very dilute aqueous solutions, the results are only approximate.

$$c = 0{\cdot}72,\ l = 2,\ \alpha^{20^\circ} = +1{\cdot}36^\circ, \text{ hence } [\alpha]_D^{20^\circ} = +94{\cdot}44^\circ.$$

The amide was prepared with the object of obtaining the imide from it by the action of heat, as an examination of this substance, it was thought, would throw some light on the influence of ring formation on optical activity. The amide did not suffer any loss of weight when heated to 160° in an air-bath, but when heated strongly in a test-tube it fused and volatilised with a considerable evolution of ammonia and some charring. By distillation in a vacuum on a graphite bath, the substance entirely sublimed without fusion or charring in beautiful needles an inch long, which resembled the original substance in respect of insolubility and difficult fusibility, but showed a considerably higher specific rotation, namely, +105·9°. A combustion giving C = 40·80, H = 7·18 per cent. proved

however, that the substance was unaltered amide, the high rotation being due probably to the presence of a small quantity of some more active product.

Metallic d-*Dimethoxysuccinates.*

The diammonium and ammonium hydrogen salts both crystallise readily, the former in needles, the latter in prisms. The dipotassium salt is very soluble, and was not obtained in definite crystals; the hydrogen potassium salt crystallises in radiating needles. The silver salt is very soluble in water and decomposes when its solution is evaporated. The magnesium salt on evaporating its solution leaves a gum, which solidifies to a glass. The following salts, whose rotatory powers were observed, were analysed; the numbers given are the percentages of metal in the dehydrated salt.

Disodium Salt.—Feathery aggregates very soluble in water. Found Na = 20·80; calculated 20·72 per cent.

Sodium Hydrogen Salt.—Minute prisms, less soluble than the normal salt, anhydrous at 100°. Found, Na = 11·36; calculated, 11·50 per cent.

Barium Salt.—Well developed, short prisms containing 5 mols. of water of crystallisation; sparingly soluble in water. Loss of water at 168°; H_2O = 22·27; $5H_2O$ requires 22·31. Found, Ba = 43·65, 43·72; calculated, 43·84 per cent. One hundred c.c. of an aqueous solution saturated at 20° contained 1·38 grams of anhydrous salt.

Calcium Salt.—Prisms, fairly soluble, containing 2 mols. of water of crystallisation, which are given off entirely only at about 160°. Loss of water; H_2O = 14·62, 14·22; $2H_2O$ requires 14·28. Found, Ca = 18·55, 18·47; calculated, 18·52 per cent.

Zinc Salt.—Aggregates of prisms, containing 2 mols. of water of crystallisation, which are lost at 160°. Loss of water; H_2O = 12·88; $2H_2O$ requires 12·98. Found, Zn = 26·71, 27·03; calculated, 27·09. A solution saturated at 20° contains about 4·4 per cent. of anhydrous salt.

The rotations of the acid and its metallic salts in solution are tabulated below. The observations were taken at 20° in a 2 dcm. tube. One or more solutions of each substance were prepared, and the others of different concentration were procured from these by dilution; in the case of the acid and the sodium hydrogen salt, the quantities used were weighed, and the solutions made up to known volumes at 20°, but in the case of the other salts, as they could not be dehydrated without a risk of impairing the activity, the concentrations were ascertained by weighing the dry residues left on evaporating known volumes, and controlling the result by estimating the metal by incineration. The acid and salts were in general examined in solutions of nearly equivalent strength; the approximate concentrations with

respect to anhydrous substance, in terms of a normal solution, are given in the column headed *N*.

Rotatory powers of solutions of d-*dimethoxysuccinic acid and its salts.*

Substance.	Solvent.	*C*.	*N*.	$[\alpha]_D^{20°}$.	$[\alpha]_D^{20°}\frac{M}{100}$.
Acid	Acetone	8·9091	1	+89·29°	+158·9°
,,	,,	3·5595	$\frac{2}{5}$	91·30	162·5
,,	,,	1·7797	$\frac{1}{5}$	95·80	170·5
,,	Water	17·5839	2	72·28	128·7
,,	,,	8·9104	1	74·74	133·0
,,	,,	4·4570	$\frac{1}{2}$	75·39	134·2
,,	,,	1·7812	$\frac{1}{5}$	76·63	136·4
Sodium hydrogen salt.	,,	10·0116	1	57·03	114·1
,,	,,	5·0078	$\frac{1}{2}$	57·31	114·6
,,	,,	2·0000	$\frac{1}{5}$	58·50	117·0
Disodium salt	,,	10·1755	1	52·68	117·0
,,	,,	5·0830	$\frac{1}{2}$	53·02	117·7
,,	,,	2·0370	$\frac{1}{5}$	54·00	119·9
Barium salt	,,	1·3775	—	27·22	85·2
Calcium salt	,,	10·6535	1	42·38	91·5
,,	,,	5·3160	$\frac{1}{2}$	43·83	94·7
,,	,,	2·1350	$\frac{1}{5}$	46·37	100·2
Zinc salt	,,	4·3690	—	−5·95	−14·4
,,	,,	2·1845	—	+6·18	+14·9
,,	,,	1·0923	—	17·39	42·0
,,	,,	0·5461	—	36·62	88·4

Discussion of Results. Ethereal Dimethoxysuccinates.

The ethereal tartrates, like the malates and lactates, exhibit a remarkable rise of optical activity when their alcoholic hydroxyl is alkylated. It seems probable that the alkylation with silver oxide and alkyl iodide is effected by simple substitution, possibly through the formation of an intermediate unstable silver derivative, and it is therefore very unlikely that any inversion of configuration occurs, such as Walden encountered in the interconversion of malic and chlorosuccinic acids. As, however, in the opinion of its discoverer (*Ber.*, 1899, 32, 1864), the change of configuration in this case occurs during the hydrolysis of the halogen-succinic acid by silver oxide, and as this reagent was also used in our method of alkylation, we thought it well to assure ourselves that no inversion had taken place, by reconverting the dialkyloxysuccinic acid into tartaric acid. It will be seen in the succeeding paper that by the action of hydriodic acid on dimethoxysuccinic acid *d*-tartaric acid is produced. The ethereal tartrates and dialkyloxysuccinates of similar sign of rotation possess therefore a similar configuration, and the effect of alkylating the tartrates is to largely increase the dextro-rotation. This effect differs in a marked

degree from that produced by the introduction of acyl groups into the tartrates, which either alters the rotation in the positive sense comparatively slightly, or more frequently produces an effect in the opposite direction.

It is now generally recognised that the influence of substitution on the optical activity of a compound depends more on the chemical nature of the introduced group than on its mass, and that radicles of a like kind cause changes of rotation which are similar with respect to direction, and similar also, in a general sense, quantitatively. This point has been brought forward prominently in recent communications to this Journal by Frankland and his pupils (Trans., 1900, **77**, 1108; 1901, **79**, 511), and by Guye (Trans., 1901, **79**, 475). The following data selected chiefly from Frankland's paper (*loc. cit.*), to which we add our own observations on mono- and di-alkyloxysuccinates, will suffice to show the relative effects of the introduction of alkyl and acyl groups into ethyl tartrate and malate. To facilitate the comparison of the two series of compounds, we have halved the molecular rotations of the tartrate derivatives, and have regarded the malic compounds as derived from *d*-malic acid, the stereo-chemical analogue of *d*-tartaric acid.

Malic derivatives.	$t°$.	$[M]_D$.	Tartaric derivatives.	$t°$.	$\frac{[M]_D}{2}$.
Ethyl monoethoxysuccinate *	17°	+121·0°	Ethyl diethoxysuccinate ‡	18°	+122·1°
Ethyl monomethoxysuccinate *	18	102·2	Ethyl dimethoxysuccinate	20	105·3
			Ethyl diphenacetyltartrate	20	39·6
Ethyl bromoacetylmalate	20	69·9	Ethyl dimonochloroacetyltartrate	,,	12·8
Ethyl acetylmalate †	,,	52·4	Ethyl diacetyltartrate	,,	4·95
Ethyl malate †	,,	20·2	Ethyl tartrate	,,	7·93
Ethyl benzoylmalate	21	11·4	Ethyl dibenzoyltartrate	,,	−123·6
Ethyl *p*-toluylmalate	20	0·68	Ethyl di-*p*-toluyltartrate	,,	−242·2

* Trans., 1895, **67**, 979.

† *Zeit. physikal. Chem.*, 1895, **16**, 495.

‡ Trans., 1899, **75**, 159. A later preparation of this compound shows that the rotation given is probably about 2° too low.

It will be seen that, with respect to their influence on the rotation of both malate and tartrate, the alkyl radicles stand at the positive, the aromatic acyl groups at the negative, end of the scale, whilst the fatty acyl groups, including phenacetyl, hold an intermediate position. The effects of the substitution of the hydroxylic hydrogen of the ethereal lactates by alkyl radicles (Trans., 1899, **75**, 487), and by benzoyl and acetyl radicles (Proc., 1895, **11**, 54), show a similar relation.

Considering the members of the tartaric series as derived from the corresponding malic compounds by the introduction of OR into the group $CH_2 \cdot CO_2Et$, it might be supposed that this substitution, occurring not in immediate proximity to the asymmetric carbon atom, would possibly not affect the rotation greatly. The supposition proves, in fact, to be correct with respect to the introduction of the alkyloxy-radicle into the monoalkyloxysuccinate, the dialkyloxysuccinates having, as will be seen, approximately the same rotation as the monoalkyloxysuccinates. The introduction of hydroxyl, on the other hand, into ethyl malate, or of an acyloxy-group into the corresponding acylmalate, produces a marked effect, which shows itself in the rotations of the tartrate and its derivatives by a general shifting of the values in the lævo-direction. That is to say, the rotation of the monoalkyloxysuccinate is scarcely affected by the introduction of a second alkyloxy-group; the dextro-rotation of the malate is considerably reduced by the introduction of another hydroxyl group, whilst with the acylmalates the effect of the substitution is still greater in the same direction, the slight dextro-rotation, for instance, of the *p*-toluylmalate becoming a powerful lævo-rotation in the di-*p*-toluyltartrate. It is impossible at present to offer any explanation of this difference in the behaviour of the monoalkyloxysuccinates and acylmalates with respect to the effect of further substitution; it may be due either to the difference in the nature of the introduced groups or to the different states of dissymmetry of the parent monosubstituted compounds, or to both causes combined.

In view of recent researches, and more particularly of Frankland's exhaustive survey of the known homologous series of optically active compounds, which exhibit a maximum rotation (Trans., 1899, **75**, 347), it must be admitted that the attempt to find a relation between Guye's product of asymmetry and the rotatory powers of compounds has not met with success, and will probably have to be abandoned. Although failure has attended this attempt, the more general form of the original conception put forward by Guye and Crum Brown still survives, and may serve as a guide in research. According to this conception, the measure of rotatory power may still be represented as the product of the differences of each pair of four coefficients, the values of which, however, are conditioned by other factors besides mass, and a progressive variation in the value of one of these may result in the occurrence of maxima of rotation. Homologous series, therefore, in which the phenomenon of a maximum rotation is found, still deserve particular attention.

It will be seen, from our observations tabulated below, that the specific rotations of the three dimethoxysuccinic esters at 60° show a distinct maximum at the ethyl term.

Ethereal dimethoxysuccinates.

	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.	$[\alpha]_D^{60°}$.	$[M]_D^{60°}$.	Mol. vol. calculated for 15°.	Mol. vol. experimental.
Methyl.....	—	—	82·5	170·0	181·5°	182·0 (60°)
Ethyl.....	90·0	210·6	85·4	199·8	213·7	212·3 (15°)
Propyl	84·9	222·4	81·1	212·5	245·9	246·9 (20°)

It was impossible to take observations on the methyl ester at lower temperatures, but even if the rise of rotation attending the fall of temperature from 60° to 20° were greater for this compound than for the other two, which might be the case, the maximum rotation exhibited by the ethyl term would probably still persist at 20°.

Frankland (*loc. cit.*) concludes, from certain considerations, alluded to below, that the maxima of specific rotation exhibited by the ethereal malates and lactates are probably attributable to the depression of the rotations of the lower members of the series by molecular association. The maximum exhibited by the dimethoxysuccinates cannot, however, be accounted for in this way. The methyl ester, it is true, according to Traube's method of calculating association factors, should be considerably associated at 20°, as its experimental molecular volume, even at 60° (see the Table), is only just in excess of the value calculated from his constants, which refer to 15°, and the ethyl term is little, if at all, associated at the lower temperature. It is shown, however, in the succeeding paper (p. 973), that the specific rotation of the methyl ester at 20° in water is 78·5°, and that the substance under these conditions has a normal molecular weight; that is to say, the dissociating solvent, water, lowers the rotation to a value even below that of the pure liquid at 60°, whilst the rotation of the ethyl compound, it was found, is little affected by water. Assuming, then, in accordance with prevalent ideas, that associated molecules are present in the pure liquid methyl ester, and that they influence the rotation, their effect would be to raise it, and, consequently, were the methyl compound in the unimolecular condition, the maximum exhibited by the ethyl term would be still more pronounced.

The molecular rotations, it will be seen, increase from the methyl term upwards but tend towards a maximum. The completed series would probably present the same phenomena as others in which a maximum occurs, of which Guye and Chavanne's amyl esters of the fatty acids (*Bull. Soc. Chim.*, [iii], 1896, **15**, 183, 275), Reitter's ethyl acetylmalates (*Zeit. physikal. Chem.*, 1901, **36**, 164), and Frankland's

glycerates and diacetylglycerates (Trans., 1894, 65, 755) are typical, namely, a rise of molecular association to a maximum, which either remains nearly constant or is followed by a more gradual fall.

Frankland, in the paper already quoted, suggests that the phenomenon of maximum specific rotation exhibited by certain homologous series is probably attributable to two distinct causes; in the case of the ethereal malates and lactates, the maximum is only apparent, being reasonably explicable as due to the association of the initial terms; in that of the tartrates, glycerates and diacetylglycerates, the maximum cannot be thus accounted for, and is due to some other cause. He is led to this conclusion by the observation that, whilst ethyl malate has a higher specific rotation than methyl malate, the order of the values for the corresponding benzoyl- and toluyl-malates is reversed, this phenomenon being coincident with the fact that the malates, on the evidence of Traube's method, are associated (the methyl term, however, much more so than the ethyl term) and the acylmalates, referred to, unassociated. He finds similar relations on comparing the malates with Walden's fatty acylmalates and chlorosuccinates, and concludes that it is not improbable that the real values of $[\alpha]_D$ for the unimolecular malates diminish in passing up the series from the methyl term. A similar argument and conclusion apply to the lactates. On the other hand, the maximum rotation observable in the tartrates, glycerates, and diacetylglycerates cannot, he thinks, be thus explained, because it is so very pronounced, and because in their substitution compounds, which show little or no evidence of association, the relationship between the rotations of the methyl and ethyl esters is retained.

We doubt if the facts really warrant this explanation of the maxima of rotation presented by the malates and lactates. First, with respect to the reversed order of the specific rotations of the initial terms of the series of substituted malates, the reversal in question is not quite general. The decrease of values on ascending the series of fatty acylmalates is so slight and irregular as to be within the limit of experimental error, and the case of the chlorosuccinates cannot be cited in support of the hypothesis, if Walden's views, (*Ber.*, 1899, 32, 1864) published since Frankland's paper, are correct. In Walden's opinion, the dextrorotatory chlorosuccinates correspond in configuration to the *l*-malates, and ought, therefore, according to the hypothesis, to show an increase of rotation with ascent of the series instead of a pronounced decrease which they actually exhibit. Further, we doubt if the assumption on which the hypothesis is based is warranted. It is assumed, namely, that when a series of esters is transformed by substitution into a new series, if the supposed disturbing influence of association is absent, the members of the substituted series will present the same order of rotation values as the parent series, each rotation

being simply shifted by a certain amount in the positive or negative direction, as the case may be. This may not, however, hold true, for independently of any effect due to changed degree of association, the substitution may influence the state of dissymmetry of successive members of the series in different degrees and so produce a considerable change in the relation of their rotation values, or even reverse their order from the first term onwards. The dimethoxysuccinates present a case in point. By methylating the tartrates, the maximum specific rotation of the series is displaced from the propyl to the ethyl term, with the result that, although none of the compounds concerned are, according to Traube's method, affected by association, ethyl dimethoxysuccinate has nevertheless a higher specific rotation than the propyl compound, whilst, of the corresponding tartrates, the propyl compound has the higher rotation.

In default of more conclusive evidence, we incline to the view that, although the rotations of the initial terms of the series of malates and lactates may probably be lowered to some extent by molecular association, the maxima of rotation exhibited by them is attributable to the same causes as those of the tartrates and other series.

The discussion of this subject raises the fundamental questions of the influence of molecular association on rotation and of the trustworthiness of Traube's method of determining the association factor. In the succeeding paper, it is shown that solvents may produce marked changes of rotation without any change of association, and that association may be similarly produced without change of rotation; association evidently does not play a predominant part in the changes of rotation due to solvents, and it is extremely doubtful if it has much influence in the case of pure liquids. Traube's method of determining the association factor has not met with general acceptance, and it is doubtful how far its results may be relied on. The association factors of the lower members of a homologous series of esters determined in this manner are frequently greater than unity, and diminish gradually, on ascending the series, to the latter value; this is interpreted in discussions on optical activity as indicating gradually decreasing molecular association, but it is commonly ignored that on ascending further in the series the value of the factor does not remain constant, but continues to decrease steadily, and yet the latter phenomenon is surely equally significant with the former. This decrease can scarcely be held to indicate dissociation, and the more obvious conclusion seems to be that on ascending the series there is a gradual increase of molecular volume in excess of that due to the increase of mass, caused, it may be supposed, by a lessening of the internal forces of the liquid. The molecular expansion which accompanies the passage upwards through the lower members of a

series, such as the esters of the hydroxy-acids, is due, no doubt, partly to disgregation of associated molecules, but the expansion evidently does not cease at the term where association is supposed to disappear, but extends indefinitely through the series. This suggests a doubt whether in such series Traube's method can be relied on for ascertaining even roughly the degree of association or the point in the series where association ends.

T. S. Patterson's views on the cause of the changes of rotation produced by solution (Trans., 1901, **79**, 167, 477) suggest the idea that the changes of rotation attending the ascent of a homologous series of homogeneous liquids may also be due largely to the lessening of the internal forces, manifested in the abnormal increase of molecular volume above referred to.

Solutions of Dimethoxysuccinic Acid and its Salts.

The rotation of dimethoxysuccinic acid in aqueous solution is more constant, as was to be expected, than that of tartaric acid; it increases with dilution, like that of the hydroxy-acid, but the relative increase is much less. Dimethoxysuccinic acid, however, does not exhibit quite such a constant rotation as the monomethoxy-acid (Trans., 1895, **67**, 949), and the two acids do not show the quantitative relation presented by their ethyl esters (p. 969), half the molecular rotation of the former (68·2°) being much in excess of that of the latter acid (48·9°). The ion of the former acid, as pointed out below, is also more active than that of the latter. It is worthy of notice that in acetone solutions, on the other hand, in which the rotations of both acids are much raised, the relation in question holds good, the molecular rotation of the monomethoxy-acid (88·9°, *loc. cit.*) approximating to half that of the dimethoxy-acid (85·2°).

With respect to the salts, in dilute solution they are dextrorotatory like the acid and its esters, and their rotations increase with dilution. The calcium salt shows a much greater rise with dilution than the normal sodium salt, and the molecular rotations of both barium and calcium salts in dilute solution fall further short of the maximum molecular rotation of the sodium salt than the law of Oudemans and Landolt would lead us to expect. The monoalkyloxysuccinates show similar relations (Trans., 1893, **63**, 239). According to van 't Hoff this behaviour of the salts of bivalent metals of polybasic acids is probably attributable to the influence of ring formation, as well as to less advanced electrolytic dissociation. This view is supported by the fact that the molecular rotations of the corresponding salts of the monobasic alkyloxypropionic acids (Trans., 1899, **75**. 490), approximate much more closely to the maximum. On the other hand, the remark-

able behaviour of zinc dimethoxysuccinnate, which even in a 4 per cent. solution is already lævorotatory, is not to be accounted for as van't Hoff suggests, as the zinc alkyloxypropionates (*loc. cit.*) show a similar abnormally rapid change of rotation with change of concentration. The known low degree of electrolytic dissociation of zinc salts (*Zeit. physikal. Chem.*, 1898, 27, 399), and hydrolytic dissociation are probably the disturbing factors here.

The rotations of aqueous solutions of the mono- and di-alkyloxysuccinic acids and their salts show some further relations which deserve notice; these may be seen from the following data abstracted from the present and previous papers (Trans., 1893, 63, 239; 1895, 67, 955; 1899, 75, 159). The numbers quoted are molecular rotations, halved in the case of the dialkyloxysuccinic compounds, and the differences given are the percentage rises of rotation between successive terms in ascending the series.

Mono- and di-alkyloxysuccinic acids.

	Acid.	Diff.	Hydrogen alkali salt.	Diff.	Normal alkali salt.	Diff.
Monomethoxysuccinic ...	48·9°		43·6°		21·4°	
		7·8°		32·6°		67·8°
Monoethoxysuccinic	52·7		57·8		35·9	
		21·0		19·7		21·2
Monopropyloxysuccinic...	63·8		69·2		43·5	
Dimethoxysuccinic.....	68·2		58·5		59·9	
Diethoxysuccinic	68·5		—		51·4	

The ethereal monoalkyloxysuccinates (Trans., 1895, 67, 979) exhibit a rise of molecular rotation in passing from the methoxy- to the corresponding ethoxy-compounds; the esters of the propyloxy-acid have not yet been prepared, but it is probable that the increase will still continue to this term of the series. In agreement with the esters, the monoalkyloxy-acids, acid salts, and normal salts, as will be seen from the table, show also a rise of molecular rotation on ascending the series. The rise between the ethoxy- and propyloxy-compounds is uniform, namely, 20—21 per cent. whether acids, acid salts, or normal salts are considered, but the relations of the methoxy- to the ethoxy-compounds are quite different, the rise here being much less for the acids (7·8), much greater for the acid salts (32·6), and still greater for the normal salts (67·8). The effect of the methoxy-group, as compared with that of the higher alkyloxy-radicles, is to raise the rotation of the slightly dissociated acid and to lower the rotation of its ion. This effect of the lowest term of this series of radicles in raising the rota-

tion of the acid in aqueous solution is of some interest, as it explains similar perplexing relations encountered in the alkyloxypropionates (Trans., 1899, 75, 490; 1898, 73, 874). The following diagram represents the relations of the alkyloxypropionic compounds with respect to the values of their molecular rotations, so far as they have been studied :

Methoxy-ion < ethoxy-ion < propyloxy-ion (aqueous solution).
Methoxy-acid > ethoxy-acid < propyloxy-acid („)
Methoxy-acid > ethoxy-acid (liquid).
Methoxy-esters > ethoxy-esters („)

The difference found between the rotations of the methoxy- and ethoxy-acids in the liquid state was very slight, but in general it may be said that in the case of the undissociated esters and slightly dissociated acids, particularly in the presence of water, the methoxyl group has a peculiar effect in raising the optical activity.

With respect to the dialkyloxysuccinic compounds, the methoxy-esters are less active than the ethoxy-esters, so far as these have been examined, and it might have been expected that aqueous solutions of the two acids would show the same relation, but here again the peculiar effect of the methoxyl group asserts itself, with the result that the acids have nearly the same molecular rotation ; in contradistinction to what might have been expected from the relations of the monoalkyloxysuccinic acids, which have been indicated above, the effect of the methoxyl group in raising the rotation extends to the ion of dimethoxysuccinic acid, sodium dimethoxysuccinate having a higher molecular rotation than the corresponding diethoxy-salt.

In conclusion, we point out a general relation which seems to hold between the hydroxy-acids and the corresponding alkyloxy-acids, which has been alluded to in previous papers (Trans., 1899, 75, 160), and finds further illustration in tartaric and dimethoxysuccinic acids. The molecular rotations of dilute aqueous solutions of the normal *d*-malates, *d*-lactates, and *d*-tartates are much higher in the dextro-sense than those of the corresponding free acids ; in the case of the alkylated derivatives, on the other hand, the rotations of the normal alkali salts are much lower, or, at most, only slightly higher, than those of the free acids ; that is to say, the rise of rotation produced by alkylation tells much more strongly on the hydroxy-acids than on their salts. The known marked influence of hydroxyl groups on the physical properties of compounds, and the great effect of varying concentration on the rotation of aqueous solutions of the hydroxy-acids, suggests that the cause of the general relation just indicated is to be sought for in some peculiarity of the latter acids, which has the effect of lowering their optical activity.

We are at present engaged in an investigation of the higher members

of the series of dialkyloxysuccinic acids and their derivatives, which we hope may throw some light on the relations of the members of the group with respect to optical activity.

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CIII.—*The Influence of Solvents on the Rotatory Powers of Ethereal Dimethoxysuccinates and Tartrates.*

By Thomas Purdie, F.R.S., and William Barbour, B.Sc., Berry Scholar in Science.

The observations recorded in this paper were made with the view of comparing the effect of solvents on the rotations of ethereal tartrates and their alkylated derivatives, the ethereal dimethoxysuccinates. The facts already known concerning the influence of solvents on optical activity, more particularly the extended observations of Freundler on the ethereal diacyl tartrates (*Ann. Chim. Phys.*, 1895, [vii], 4, 235), and the recent systematic investigation by Patterson (Trans., 1901, 79, 167, 477) of the influence of various solvents on ethyl tartrate, suffice to show that the action in question, even in the case of non-electrolytes, is very complex, and that at present no general theory on the subject can be formulated.

The phenomena presented by the esters of tartaric and other hydroxy-acids are probably much complicated by the presence of the hydroxyl group, which is well known to exercise a marked influence on physical properties in general, and it appears from Freundler's researches that, even when the hydroxyl is acylated, variations of optical activity occur under the action of solvents, for which it is difficult to discover a satisfactory explanation. Freundler, for instance, was led to conclude that the effect of benzene on the rotations of the diacyltartrates was connected with a peculiar form of dissociation, in which the acyl groups were split off from the compounds. It seems probable that the alkylated esters of hydroxy-acids should present phenomena of a less complex kind, and that they should be less subject, at all events, to the possible disturbing effects of molecular association than the parent esters. We purpose, therefore, investigating the action of solvents on the rotations of mono- and di-alkyloxysuccinic and alkyloxypropionic esters, and in the present preliminary paper we record observations on solutions of the three dimethoxysuccinic esters described in the preceding communication, in water, methyl alcohol and benzene. We

have also made some observations on solutions of the corresponding tartrates, but have refrained from proceeding further with these compounds, as we understand that Mr. Patterson's investigation, alluded to above, will include the whole series of tartaric esters.

Conversion of d-*Dimethoxysuccinic Acid into* d-*Tartaric Acid.*

For a comparison of the rotations of the tartaric and dialkyloxysuccinic esters, it is essential that the relationship of the two classes of compounds, with respect to configuration, should be known with certainty. As indicated in the preceding paper, it is very improbable that in the process of alkylating the esters of optically active hydroxy-acids with alkyl iodide and silver oxide, any inversion of configuration occurs, but we thought it well, nevertheless, to set the question at rest by reconverting dimethoxysuccinic acid into tartaric acid.

5·5 grams of *d*-dimethoxysuccinic acid were accordingly heated with ten times the weight of fuming hydriodic acid in a sealed tube at 100° for 8 hours. The production of an oily layer, smelling of alkyl iodide, indicated that the desired reaction had occurred. The aqueous layer, after most of the hydriodic acid had been removed from it by heating in a vacuum, deposited a crystalline acid on standing in a desiccator over potash; this, after washing with ether to remove iodine and recrystallising from water, melted at 167°. The melting point of tartaric acid is 167—170°. A determination of the specific rotation in aqueous solution at 20° gave $c = 4·097$, $l = 2$, $\alpha = +1·24°$, $[\alpha]_D^{20°} = +15·13°$. According to Landolt (*Ber.*, 1873, **6**, 1075), the specific rotation of tartaric acid under these conditions is 14·52°. The sparingly soluble potassium hydrogen salt of the acid gave in aqueous solution at 20° $c = 0·615$, $l = 4$, $\alpha = +0·56°$, $[\alpha]_D^{20°} = +22·76°$, the value quoted by Landolt for potassium hydrogen tartrate at the same concentration being +22·61°. On analysis, the salt gave

C = 25·66; H = 2·80; K = 20·47, 20·84.

$C_4H_5O_6K$ requires C = 25·51; H = 2·66; K = 20·81 per cent.

d-Dimethoxysuccinic acid yields *d*-tartaric acid by the treatment described, and as the esters in both cases are active in the same sense as their acids, it follows that ethereal dimethoxysuccinates and tartrates of similar sign of rotation have the same configuration.

In the tables below, we give the results of our polarimetic observations. The dimethoxysuccinic esters used were prepared in the same manner as the specimens described in the preceding paper, and, as will be seen from the numbers quoted, they showed practically the same specific rotations as the previous preparations. The tartrates used were obtained from Kahlbaum, and purified by fractional dis-

tillation. In calculating the specific rotation of these esters, the specific gravities quoted by Pictet were used. The observations were taken in a 2 dcm. tube at 20°. The specific gravity of the benzene used in the solutions was $d\ 20°/4° = 0·8785$. The methyl alcohol employed was Kahlbaum's, dried by distillation from calcium oxide and from sodium; the specimen used in the observations on methyl dimethoxysuccinate had the specific gravity $d\ 20°/4° = 0·7927$, but that used in the other observations, having accidentally absorbed moisture, had the specific gravity 0·7946. The concentration, c (grams of substance in 100 c.c. of solution), was determined in a few instances by making up the solution of a weighed quantity of substance to a known volume, but in most cases it was found from p (grams of substance in 100 grams of solution), and the specific gravity of the solution $d\ 20°/4°$.

Methyl Dimethoxysuccinate.

It was found impossible to take observations on the pure ester in the superfused state, but the following approximate data may be quoted, which are calculated from observations at 60° on the assumption that the changes with temperature are the same as in the case of the ethyl ester.

$$[\alpha]_D^{20°} = +87°,\ [M]_D^{20°} = +179·2°,\ d\ 20°/4° = 1·1751,\ \frac{M}{d} = 175·3.$$

Solvent.	c.	$d\ 20°/4°$.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.	Mol. sol. vol.
Water	19·9988	—	+78·71°	+162·1	—
,, ...	10·0315	—	78·45	161·6	—
,, ...	5·0319	—	78·50	161·7	—
Benzene	20·0036	—	101·63	209·4	—
,, ...	10·0128	—	104·66	215·6	—
,, ...	5·0060	—	105·47	217·3	—
	p.				
,, ...	11·1694	0·9033	104·42	215·1	176·9
Methyl alcohol	23·0151	0·8591	78·90	162·5	172·6
,, ,, ...	12·0806	0·8276	76·32	157·2	169·2
,, ,, ...	6·2598	0·8102	81·04	166·9	170·2

Ethyl dimethoxysuccinate.

$[\alpha]_D^{20°} = +89·7°$, $[M]_D^{20°} = +209·9°$, $d\ 20°/4° = 1·0975$, $\frac{M}{d} = 213·2$.

Solvent.	c.	d 20°/4°.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.	Mol. sol. vol.
Water	5·3752	—	+89·11°	+208·5°	—
	p.				
Methyl alcohol	19·0407	0·8407	87·27	204·2	209·7
,, ,,	9·7365	0·8178	87·41	204·5	208·7
,, ,,	6·0569	0·8089	87·66	205·1	208·5
Benzene	19·3137	0·9142	102·65	240·2	212·5
,,	10·1117	0·8969	104·14	243·7	212·3
,,	5·3130	0·8879	104·93	245·5	213·3

Propyl dimethoxysuccinate.

$[\alpha]_D^{20°} = +84·9°$, $[M]_D^{20°} = +222·4°$, $d\ 20°/4° = 1·0608$, $\frac{M}{d} = 247·0$.

Solvent.	p.	d 20°/4°.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.	Mol. sol. vol.
Methyl alcohol	23·7085	0·8479	+85·79°	+224·8°	242·3
,, ,,	12·3697	0·8213	84·50	221·4	243·1
,, ,,	6·6571	0·8086	84·99	222·7	244·0
Benzene	21·5619	0·9136	99·24	260·0	245·1
,,	11·4730	0·8966	101·00	264·6	245·7
,,	5·6932	0·8873	101·26	265·3	246·3

Methyl tartrate.

$[\alpha]_D^{20°} = +2·14°$, $[M]_D^{20°} = +3·8°$, $d\ 20°/4° = 1·3284$, $\frac{M}{d} = 134·0$.

Solvent.	p.	d 20°/4°.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.	Mol. sol. vol.
Water	5·0231	1·0131	+20·04°	+35·7°	126·3

Ethyl tartrate.

$[\alpha]_D^{20°} = +7·62°$, $[M]_D^{20°} = +15·7°$, $d\ 20°/4° = 1·2059$, $\frac{M}{d} = 170·8$.

Solvent.	p.	d 20°/4°.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.	Mol. sol. vol.
Benzene	21·0627	0·9308	+6·12°	+12·6°	171·9
,,	10·7339	0·9038	6·29	13·0	173·4
,,	5·6479	0·8913	6·75	13·9	174·9

Propyl tartrate.

$[\alpha]_D^{20°} = +12{\cdot}31°$, $[M]_D^{20°} = +28{\cdot}81°$, $d\ 20°/4° = 1{\cdot}1344$, $\frac{M}{d} = 206{\cdot}3$.

Solvent.	p.	$d\ 20°/4°$.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.	Mol. sol. vol.
Water	4·8206	1·0071	+26·67°	+62·4°	191·7
Benzene	22·2112	0·9257	18·31	42·8	205·2
,,	11·1266	0·8993	20·34	47·6	211·0
,,	5·4685	0·8890	20·78	48·6	208·8*
,,	5·6205	0·8886	19·62	45·9	212·5†

* This number for molecular solution-volume is probably too low.

† The specific rotation found by Freundler in about a 5 per cent. solution was +20·1°.

So far as the available data go, it may be said that, in general, the rotations of the dimethoxysuccinates are less affected by solvents than those of the corresponding tartrates, and that the action is in most cases oppositely directed. The following table in illustration of the statement shows the changes produced on the molecular rotations by the solvents mentioned at concentrations of about 5 per cent., a rise or fall of dextro-rotation being indicated by + or − respectively.

Solvent.	Tartrate.	Dimethoxysuccinate.
Water	Methyl +31·9°	−17·5°
,,	Ethyl +38·2 *	−1·4
,,	Propyl +33·6	slightly affected ‡
Methyl alcohol	Ethyl +7·9 *	−4·8°
Benzene	Methyl −19·5 †	+38·1

* Patterson (*loc. cit.*).

† Freundler (*loc. cit.*).

‡ The ester is very slightly soluble in water, and the conclusion is based on an observation made in aqueous methyl alcohol.

Attention may be drawn to the following facts concerning the dimethoxysuccinates. The three esters examined undergo a considerable rise of rotation when dissolved in benzene, and the rotations increase with dilution, the lowest member of the series being most affected by the initial action of the solvent, and also most affected by change of concentration. The greater influence of the benzene on the first member of the series results in the extinction of the maximum specific rotation at the ethyl term, which is shown by the pure esters.

The effect of water and of methyl alcohol on the rotations of the three esters is, in general, in the opposite sense to that of benzene, and the first member of the series is again most affected. The rotation in water, unlike that in benzene, is scarcely affected by change of concentration, at least from 20 per cent. downwards. The observations on these esters in methyl alcohol present two points which are worthy of notice. First, the rotation-concentration curves of the methyl and propyl compounds exhibit a minimum, more pronounced in the curve of the former, between the concentrations of 20 and 5 per cent., a peculiar phenomenon of which Patterson (*loc. cit.*) has found striking examples in certain solutions of ethyl tartrate. The absence of a corresponding minimum in our ethyl ester is probably due to the range of concentration examined, in the case of this compound being less than in that of its two homologues. Secondly, it will be seen that whilst methyl alcohol lowers the rotations of the methyl and ethyl esters at all the concentrations examined, it slightly raises that of the propyl ester at a concentration of 20 per cent. This peculiarity is referred to below. Finally, it may be remarked that, owing to the greater lowering effect of methyl alcohol on the first member of the series, the specific rotations of the three compounds in this solvent exhibit a more pronounced maximum at the ethyl term than those of the liquid esters.

Turning to the tartrates, Freundler (*loc. cit.*) has shown that benzene in 5 per cent. solutions lowers the specific dextro-rotation of the methyl ester from $+2{\cdot}14°$ to $-8{\cdot}8°$, but raises that of the propyl compound from $+12{\cdot}44°$ to $+20{\cdot}1°$. He remarks, with regard to these effects, that they are entirely irregular. It seemed to us very remarkable that the rotations of two closely related members of the same homologous series should be influenced to such a marked degree in opposite directions by the same solvent, and we therefore examined the effect of benzene on the intermediate ethyl ester, and also made further observations on the propyl ester in the same solvent. Our results with the latter compound confirm those of Freundler, and show besides that the rotation increases somewhat on dilution. We find that, with respect to the effect of benzene, the behaviour of the ethyl ester is intermediate between that of its two adjoining homologues. The specific rotation is only about 1° less than that of the pure compound, and is but little affected by concentration. The effect of methyl alcohol on the dimethoxysuccinates, referred to above, gives indications of a similar reversal of the influence of the solvent on ascending a homologous series, and we are led to think that the phenomenon, to which, so far as we know, attention has not hitherto been drawn, will be found to be one of general occurrence. Freundler's data (*loc. cit.*) furnish a number of examples,

of which the propyl diacetyl-, dibutyryl-, and dihexoyl-tartrates may be mentioned.

	Diacetyl-, $[\alpha]_D$.	Dibutyryl-, $[\alpha]_D$.	Dihexoyl-tartrate, $[\alpha]_D$.
Pure ester	+13·4°	+5·2°	+2·2°
Solution in methyl alcohol..	12·1	9·3	5·4
„ acetone	10·4	7·2	5·3
„ ethyl alcohol ...	9·6	6·3	3·6

Similarly, for the diacetyltartrates, alcohol and acetone lower the rotations of the ethyl and propyl and raise that of the butyl ester; also for the dipropionyltartrates, the same solvents lower the dextrorotation of the methyl ester, and raise that of the ethyl ester. Other available data indicate that, on ascending a homologous series, the effect of the solvent on the rotations tends, at least, towards a minimum, and would probably become reversed at a higher point in the series; Patterson's observations on ethyl tartrate, and our own on the methyl and propyl esters in 5 per cent. aqueous solution at 20°, afford an example, thus:

	Methyl, $[\alpha]_D$.	Ethyl, $[\alpha]_D$.	Propyl, $[\alpha]_D$.
Pure ester	+2·1°	7·6°	12·3°
Solution in water	20·0	26·2	26·7

The cause of the phenomenon referred to is probably related to that which determines the occurrence of a maximum rotation in a homologous series of liquid compounds. It might be expected that the relation between the effects produced on the initial members of a series by the action of a solvent and by the addition of CH_2 to the active molecule of the pure liquid would be retained throughout the series, and that the effect of the solvent, like that of the addition of CH_2, would therefore be reversed about the point of maximum rotation. In the case of the tartrates, the reversal of the effect of benzene and the maximum rotation occur, as a fact, at the same, namely, the propyl term. In general, however, the points of reversal of the influence of the solvent and of maximum rotation do not coincide. Thus, if the effect of water on the rotations of the tartrates undergoes reversal, it must be at a term higher than that of the maximum rotation; the same is possibly the case in the series of propyl diacyltartrates quoted above, where, as the rotations decrease from the diacetyl term upwards, it is perhaps admissible to conceive that the point of maximum rotation lies at or below this term. Although the facts mentioned seem to us to indicate a connection between the effect of solvents and that of the addition of mass on the rotations of the successive members of a homologous series, it does not follow that the

mechanism of the actions in altering the state of dissymmetry of the active molecules is the same, and it is therefore not to be expected that the points of maximum rotation and reversal of the effect of the solvent should coincide.

We give below the results of a number of molecular weight determinations by the freezing point method in water and benzene, made with the view of discovering, if possible, a connection between the influence of the solvents on rotation and the molecular association of the dissolved active substance. S denotes the number of grams of substance in 100 grams of solvent.

Solvent.	*S.*	*M.*
Methyl dimethoxysuccinate. $M=206$.		
Water	3·6050	190·9
,,	7·7713	193·8
,,	12·7460	188·4
Benzene	0·8853	193·7
,,	2·4970	195·4
,,	4·6370	203·8
Ethylene dibromide.	0·6788	202·8
,, ,,	1·5300	213·2
,, ,,	2·3630	216·8
Methyl tartrate. $M=178$.		
Water	6·6313	175·3
,,	5·1511	176·4
,,	9·9887	173·4
Propyl tartrate. $M=234$.		
Benzene	1·8194	255·4
,,	3·8933	296·2
,,	7·5564	342·8
Ethyl dimethoxysuccinate. $M=234$.		
Benzene	3·3735	215·8
,,	5·0373	219·4
,,	9·0774	225·0
Propyl dimethoxysuccinate. $M=262$.		
Benzene	1·6377	231·9
,,	3·4079	236·9
,,	7·2093	241·3
,,	7·8837	244·3
Ethyl tartrate. $M=206$.		
Benzene	1·0649	220·2
,,	3·7210	281·4
,,	4·9748	299·8

Freundler, it is well known, found that in a number of substances normal molecular weight in solution was accompanied by normal rotation, abnormal molecular weight by abnormal rotation. Patterson (*loc. cit.*) has shown, however, in the case of ethyl tartrate in various solvents, that normal molecular weight may coexist with abnormal rotation, and our observations furnish various instances of the same kind. The rotations of the three dimethoxysuccinates are considerably raised by benzene, and that of the methyl ester lowered by water, but the molecular weights are normal in these solvents so far

as the freezing point method can detect. Water increases the rotation of methyl tartrate by about ten times the value of the constant of the pure compound, but the molecular weight is nevertheless normal. The change here, it is true, may be due to depolymerisation, but the similar effect produced by water on the rotation of propyl tartrate cannot be thus explained, as there is no reason to believe that this ester in the pure state is associated. Ethyl tartrate in a 5 per cent. benzene solution presents an exception to Freundler's rule of another kind, for nearly normal rotation is here associated with distinctly abnormal molecular weight.

The molecular weight determinations given above, and those by Freundler (*loc. cit.*), show that the tartrates, owing, no doubt, to the presence of the hydroxyl group, are subject to extensive molecular association, even in comparatively dilute benzene solutions, and that in the alkylated esters this tendency to association entirely disappears. If molecular association is a predominant factor in the changes of rotation produced by solution, it should be clearly manifested in the rotations of the two closely-related classes of esters in the solvent mentioned. Such, however, is not the case. The rotations of the dimethoxysuccinates, as already mentioned, are considerably increased by benzene, and those of the tartrates are modified in a manner that cannot be accounted for by the simple aggregation of active molecules as they exist in the pure liquid compounds. Methyl tartrate in benzene (Freundler, *loc. cit.*) exhibits extensive association accompanied by depression of rotation, propyl tartrate (see our tables) association accompanied by rise of rotation, and ethyl tartrate association, increasing rapidly with concentration, accompanied by only slightly changed rotation, which varies little with concentration. The coalescence of the active molecules of the ethyl ester evidently produces little or no effect on their state of dissymmetry; it is natural to conclude that the same holds true for the molecules of its two homologues, and that the reversed effect of benzene on the rotations of the methyl and propyl esters is due mainly to an initial specific action of the solvent on the state of dissymmetry of the simple molecules of the compounds.

Patterson, in the suggestive paper already referred to, has attempted, with some considerable success, to trace a connection between the influence of solvents on rotation and the internal pressure of the liquids, and more particularly between rotation and molecular solution-volume, which, on the assumption that the change of volume on solution is suffered entirely by the dissolved substance, may be regarded as a measure of the pressure in question. Our observations are not extensive enough, and so far as the densities of the more dilute solutions are concerned, probably not accurate enough, to be employed as

in any sense a crucial test of this theory; we have, however, calculated the molecular solution volumes by the usual formula, when densities were available (see the Tables, pp. 973—975), to ascertain if the results gave any support or otherwise to his views.

For ethyl tartrate, to which so far his observations have been confined, Patterson finds that the values of the rotations in aqueous and different alcoholic solvents at infinite dilution stand in the inverse order of the molecular solution-volumes; further, that solvents, such as methyl alcohol, which raise the rotation on solution, lower the molecular volume below that of the pure compound, whilst octyl alcohol, which causes a distinct fall of the rotation, raises the molecular volume.

Dimethoxysuccinates.—The rotations of the methyl and ethyl esters are both lowered by methyl alcohol, as already stated, but the former decidedly more than the latter, while that of the propyl ester is only slightly affected. The molecular solution-volumes in this solvent are less than the molecular volumes of the pure esters. Benzene raises the rotations of all three esters considerably, but influences the molecular volumes very slightly. As exact data for the pure methyl ester at 20° are not available, in order to ascertain if any connection can be traced between rotation and molecular solution-volume in this group, we have compared the effects produced on the two constants by methyl alcohol and benzene respectively. We give below the differences between the molecular rotation and molecular solution-volume of each ester in the two solvents in about 10 per cent. solutions at 20°.

	Diff. $[M]_D^{20°}$.	Diff. M.S.V.
Methyl ester	57·9°	7·7°
Ethyl „	39·2	3·6
Propyl „	43·2	2·6

These figures certainly indicate a connection between the constants. The methyl ester, which shows the greatest difference of rotation, also gives the greatest difference of molecular solution-volume. The differences of molecular solution-volume exhibited by the ethyl and propyl esters, it is true, do not stand in the same numerical order as the rotations, but the respective data for each ester approximate closely to each other, and the apparent discrepancy may well be due to slight error in determining the densities.

Our observations on the methyl ester in methyl alcohol at varying concentrations appear also to indicate a connection between the constants in question. The rotations and molecular solution-volumes vary in the same order, each showing a minimum at the 10 per cent. solution, but we do not attach great significance to this, as the range of concentration in the solutions is not sufficiently great, and the propyl ester does not show a corresponding regularity.

Tartrates.—We have refrained from proceeding further with observations on these substances, as we wished to avoid trespassing on Mr. Patterson's field of work. The following conclusions may, however, be drawn from the observations made.

The effects of solution in water on the rotations and molecular solution-volumes of methyl and propyl tartrates correspond with those found by Patterson for ethyl tartrate, namely, a notable increase of rotation and decrease of volume, but as will be seen from the numbers below, which refer to 5 per cent. solutions at 20°, no connection between the two classes of effects is apparent.

	Increase of $[M]_D^{20°}$.	Decrease of M.V.
Methyl tartrate.....	31·9°	7·7°
Ethyl ,, ...	38·2	11·9
Propyl ,, ...	33·6	14·6

The rotation of ethyl tartrate is slightly lowered by benzene, that of propyl tartrate much raised, but no corresponding change of molecular volume is evident; as in the case of ethyl tartrate in octyl alcohol, the molecular solution volumes are greater than the molecular volumes of the pure liquids, and increase with dilution.

Comparison of Ethyl Tartrate and Ethyl Dimethoxysuccinate.

Below, we give the changes of rotation and molecular volume produced by solution of these esters in methyl alcohol and in benzene at a concentration of about 5 per cent. and at 20°; numerical rise and fall are indicated by the signs + and − respectively.

	Change of $[M]_D^{20°}$.	Change of M.V.
Ethyl tartrate in methyl alcohol *.....	+7·9°	−11·5°
,, dimethoxysuccinate in methyl alcohol	−4·9	−4·7
Ethyl tartrate in benzene	−1·8	+4·1
,, dimethoxysuccinate in benzene	+35·6	unaltered

The rotation of ethyl tartrate is more raised by methyl alcohol than that of the dimethoxysuccinate is lowered, and in agreement with this the tartrate shows a greater change of molecular volume. In benzene, the tartrate also shows the greater change of molecular volume, but the effects on rotation, it will be seen, are in entire disagreement with this.

The facts given above furnish no clear evidence of a definite connection between rotation and molecular solution-volume, and we doubt if any such connection will be found to prevail generally. Patterson has pointed out several disturbing factors, which might account for the

* Patterson (*loc. cit.*).

apparently abnormal relations between rotation and molecular solution-volume which he encountered in some of his solutions. Another disturbing phenomenon suggests itself to us, which may be of frequent occurrence. Patterson's theory is based on the idea that a progressive change in the volume of an asymmetric molecule will be accompanied by a corresponding progressive change of shape, and therefore also of rotation. We doubt if this will be generally the case. According to Guye and Crum Brown, a continuous change in the value of one of the four coefficients of the groups attached to the asymmetric carbon atom, such as occurs in ascending a homologous series, may cause the rotation to oscillate between maxima on either side of the zero point. When the volume, and therefore the shape, of an asymmetric molecule is altered by the action of a solvent, no doubt the value of all four coefficients will undergo change, but one of these will probably be more subject to the action than the others. A progressive change of molecular volume, whether caused by change of concentration or by the action of a succession of different solvents, might therefore result in a periodic change of rotation. This may possibly account for what seems to be a common phenomenon, the occurrence, namely, of a point of minimum rotation in the concentration-curves of solutions of active compounds.

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CIV.—*The Occurrence of Paraffins in the Leaf of Tobacco.*

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BY the Act of 5 & 6 Vict., c. 93 (1842), manufacturers were permitted to use oil in making up spun or roll tobacco, and by the Act of 42 and 43 Vict., c. 21 (1879), the word "oil" is defined as meaning "essential oil" for the purpose of flavouring, and "olive oil" for "the process of spinning and rolling up." Prior to 1900, no legal prohibition existed as to the amount of "oil" which could be so used, but in that year it was found desirable to restrict the quantity which might be present in manufactured tobacco to 4 per cent., and by 63 & 64 Vict., c. 35 (1900), it was enacted that in calculating the proportion of oil, any fatty or oily substance which may be naturally present in the tobacco is to be included within the 4 per cent.

Discussion with manufacturers prior to the introduction of this

measure showed that it was necessary to obtain some definite knowledge concerning "the fatty or oily substance" which was alleged to be present in the natural leaf of tobacco. It was surmised by some makers that tobacco leaf not only contained such substances, but that the quantity varied with the character of leaf, conditions of growth, season, &c. At the same time, no very precise information as to the real nature of this so-called fatty or oily substance could be elicited, nor could anything relative to the subject be discovered in the already very extensive literature dealing with the natural history of tobacco.

A rapid and sufficiently accurate method of ascertaining whether the provisons of the law are complied with as regards oil consists in macerating a weighed quantity of the manufactured product with a definite volume of light petroleum, of boiling point not exceeding 60°, for about 18 hours at the ordinary temperature. An aliquot portion of the clear solution is evaporated and the residual extractive matter is dried and weighed. This is then saponified with a solution of alcoholic potash and the equivalent amount of olive oil calculated from the saponification value. Direct experiments have shown that the whole of the added oil can in this way be readily estimated, and that the results are not materially affected by the small amount of matter which the light petroleum may have extracted from the leaf.

It was, however, desirable to obtain accurate knowledge of the nature and amount of the substance or substances which light petroleum would extract from the natural leaf of tobacco. Accordingly, quantities of the various kinds of leaf used by a number of the largest manufacturers in the United Kingdom in making spun or twist tobacco were procured for examination. The samples selected consisted of some 46 representative varieties of Kentucky and Virginian-grown tobaccos, and care was taken that they corresponded in all respects with the leaf as imported; in other words, it was ensured that the tobacco was in the condition technically known as "raw leaf."

The amount of matter extracted from tobacco by light petroleum at the ordinary temperature is very small, even after prolonged maceration. In the case of the American tobaccos above-named, it varied from less than 0·5 up to about 2 per cent.; the average amount yielded by the 46 different varieties was 1·25 per cent. No glyceride, or anything in the nature of a vegetable oil or true fat, could be discovered in the extract.

Hence the apprehensions of certain manufacturers that their legal position might be prejudicially affected by the variable amount of fatty or oily matter occurring in the untreated leaf of tobacco had no foundation infact, since such substances are not naturally present in

tobacco. Experience has, in fact, amply demonstrated that the limit of oil imposed by Parliament has proved more than sufficient for the proper manufacture of spun tobacco.

The matter extracted by light petroleum from tobacco constitutes a dark brown, viscous or semi-solid substance. It is readily soluble in cold ether, carbon disulphide, chloroform, or carbon tetrachloride, but more sparingly so in absolute alcohol. On shaking with water, the aqueous solution is strongly alkaline, contains nitrogen, and gives the usual reactions for alkaloids with iodine, corrosive sublimate, and platinum tetrachloride. This alkaloid consists almost entirely of nicotine. It is present to the extent of about one-fifth of the weight of the extract. In addition, there is a small amount of wax, equal to about three-tenths of a per cent., on the original leaf, and, lastly, there are two solid hydrocarbons of the paraffin series, an account of which forms the subject of the present communication.

In order to isolate the paraffins, a quantity of the light petroleum extract obtained from several kilograms of Western Kentucky leaf, used mainly as "fillers," was dissolved in the minimum quantity of ethyl ether and the solution mixed with about six times its volume of ethyl alcohol (rectified spirit). The precipitate thus obtained was redissolved in hot alcohol, separated by cooling, and recrystallised from ether. It formed pearly, nacreous scales melting at 63·0—63·8°, and gave, on analysis,

Carbon.....	84·9 per cent.
Hydrogen	14·7 „
	99·6

showing that it was almost certainly a hydrocarbon, or mixture of hydrocarbons. That it was not a wax or solid fat was further established by boiling with standard solution of alcoholic potash. This was shown to have no action upon it, nor was the melting point of the substance at all changed.

A second preparation, from another variety of tobacco used for "wrappers," and a third preparation from leaf employed for general purposes, gave very similar results on analysis, and the products had substantially the same melting point. The actual amount of the hydrocarbon present in the leaf seemed to be fairly constant, judging from the following results:

(1) 34·92 grams of light petroleum extract obtained from 2·211 kilos. of Western Kentucky leaf gave 2·337 grams of hydrocarbon, or 0·10 per cent. on the original leaf.

(2) 28·03 grams of extract from 1·375 kilos. of Henderson tobacco gave 1·757 grams of hydrocarbon, or 0·13 per cent. on the original leaf.

(3) 106·02 grams of extract from 7·084 kilos. of leaf used for general purposes gave 8·157 grams of hydrocarbon, equal to 0·11 per cent. on the original leaf.

The amount of the hydrocarbon present in American tobacco leaf may be taken therefore as rather more than one-tenth per cent.

Although the light petroleum employed in these extractions boiled completely below 60° and left no solid residue on evaporation, it was desirable to prove that the paraffins obtained, which conceivably might exert even at 60° sufficient vapour pressure to distil over with the more volatile hydrocarbons, were not actually present in the light petroleum employed. Accordingly, about a kilogram of leaf was treated in precisely the same way with a mixture of chloroform and ether. A white substance was thus obtained resembling in all respects that extracted by the light petroleum. It melted at 64—66°, and was found on analysis to have the percentage composition :

Carbon	85·0 per cent.
Hydrogen	14·6 „
	99·6

Systematic examination of the product thus obtained showed that it was in reality a mixture. By repeated fractional crystallisation from ether it was eventually resolved into two solid hydrocarbons, which, by analysis and treatment with bromine, were recognised as paraffins.

The first hydrocarbon was found to melt at 67·8—68·5°, and gave on analysis the following numbers :

Carbon	85·1 per cent.
Hydrogen	14·8 „
	99·9

A solution in carbon tetrachloride was unaffected by bromine ($N/10$) in the same solvent, and the substance had all the characters of a hydrocarbon of the C_nH_{2n+2} series.

A determination of the molecular weight by the boiling point method, according to Beckmann, using ether as a solvent, gave values varying from 412 to 419, which agree fairly well with that demanded by the formula $C_{31}H_{64}$ (mol. wt. 436). Indeed there can be little doubt that this hydrocarbon is identical with Krafft's *hentriacontane*, $C_{31}H_{64}$, which has the melting point 68·1° (*Ber.*, 1882, **15**, 1687).

The second hydrocarbon, after repeated crystallisation from ether, in which it is markedly more soluble than the other, was found to melt constantly at 59·3—59·8°.

On analysis, it yielded :

Carbon	84·9 per cent.
Hydrogen	14·8 „
	99·7

It was entirely unaffected by a solution of bromine ($N/10$) in carbon tetrachloride, and was in other respects very similar in character to the hydrocarbon just described.

A determination of molecular weight by Beckmann's method gave somewhat higher values (433—440) than those obtained in the case of the other hydrocarbon, but the results of the analysis and the melting point indicate that the second hydrocarbon is in all probability *heptacosane*, $C_{27}H_{56}$, the melting point of which was found by Krafft to be 59·5° (*loc. cit.*).

The two paraffins appear to be present in tobacco leaf in about equal amounts and in the aggregate, as already stated, to the extent of about one part in a thousand.

We incline to the opinion that the substance obtained by Kissling (*Ber.*, 1883, **16**, 2432), and regarded by him as a wax, was in reality a mixture of the two paraffin hydrocarbons just described. Kissling, who extracted the material by means of ether, found after repeated recrystallisation from alcohol that it formed a snow-white mass of satiny lustre melting at 63°, and gave on analysis numbers agreeing with those required for the formula $C_{70}H_{140}O_2$ (C = 83·0, H = 13·8, O = 3·2 per cent.). It was present in Kentucky tobacco to the extent of 0·18 per cent.

In the course of an investigation on the constituents of tobacco smoke, Kissling also found a wax-like substance, similar in appearance to the so-called "tobacco wax," melting at 64·5°, but which seemed on analysis to be a hydrocarbon containing C = 84·7—85·5 and H = 14·63—15·16 per cent.

There can be little doubt that the substances extracted by Kissling are identical, and that they were mixtures of the paraffin hydrocarbons hentriacontane and heptacosane described in the present communication.

As present in Kentucky and Virginia leaf, we found such mixtures had the following melting points:

Western leaf	63·0—63·8°
"Wrappers"	63·5—64·0
"Fillers"	63·7—65·0

numbers almost identical with those observed by Kissling.

THE GOVERNMENT LABORATORY.
LONDON.

CV.—*Studies in the Camphane Series. Part IV. The Isomerism of α-Benzoylcamphor.*

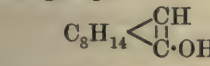
By Martin Onslow Forster.

On continuing the investigation of 1-hydroxycamphene (this vol., p. 644), attention was directed at first to its anomalous behaviour towards ferric chloride, copper acetate, and alkalis. As already mentioned, the substance in question is insoluble in caustic alkalis, its alcoholic solution does not yield a precipitate with copper acetate, and ferric chloride fails to develop a coloration with it. This inertness differentiates it quite sharply from those hydroxy-compounds representing enolic modifications of the ketonic esters studied by Claisen, W. Wislicenus, Schiff, and others, and a review of the publications of these authors at once suggested a reason for this deviation from an apparently established principle.

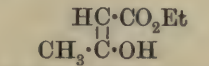
Briefly stated, it seemed probable that the peculiarity is due to the fact that 1-hydroxycamphene is the first enolic modification derived from a ketone containing a single atom of oxygen. Claisen, for example (*Annalen*, 1896, **291**, 25), has studied the behaviour of benzoyldiacetylmethane, $C_6H_5\cdot CO\cdot CH(CO\cdot CH_3)_2$, dibenzoylacetylmethane, $CH_3\cdot CO\cdot CH(CO\cdot C_6H_5)_2$, and tribenzoylmethane, $CH(CO\cdot C_6H_5)_3$, supplementing the examination of these substances by an investigation of methenyl and hydroxymethylene derivatives of ethyl acetoacetate, acetylacetone, and ethyl malonate (*Annalen*, 1897, **297**, 1). The contributions of W. Wislicenus (*Annalen*, 1896, **291**, 147) to this subject include the esters of formylphenylacetic acid, $CHO\cdot CH(C_6H_5)\cdot CO_2H$, and the isomeric forms of dibenzoylmethane (*Annalen*, 1899, **308**, 219), whilst Schiff (*Annalen*, 1899, **309**, 206) has dealt with the benzylidenebisacetylacetones, $C_6H_5CH\cdot[CH(CO\cdot CH_3)_2]_2$, amongst many others of the class under consideration.

It is unnecessary to mention more compounds belonging to this category. They display one feature in common. In each case, a complex containing oxygen is attached to the carbon atom adjacent to that united with the critical oxygen atom; in other words, the enolic modification invariably has an acidic group associated with the carbon atom contiguous to the one bearing the hydroxyl radicle.

It is this condition which is not fulfilled in the case of 1-hydroxycamphene, that substance having a single hydrogen atom in place of the acidic group,



1-Hydroxycamphene.



Enolic ethyl acetoacetate.

It appeared likely, therefore, that this might account for the singular behaviour of the substance, and with the object of putting this explanation to the proof, I attempted to prepare α-benzoylcamphor, $C_8H_{14}<\begin{matrix}CH\cdot CO\cdot C_6H_5\\ |\\ CO\end{matrix}$, expecting that 1-hydroxy-2-benzoylcamphene, the enolic modification of α-benzoylcamphor, would be found to resemble typical enolic substances :

$C_8H_{14}<\begin{matrix}C\cdot CO\cdot C_6H_5\\ ||\\ C\cdot OH\end{matrix}$ 1-Hydroxy-2-benzoylcamphene.

$\begin{matrix}HC\cdot CO\cdot C_6H_5\\ ||\\ C_6H_5\cdot C\cdot OH\end{matrix}$ Hydroxybenzylidenacetophenone.

Before proceeding to describe the process by which the enolic modification of α-benzoylcamphor has been obtained, it may be stated that the substance has all the properties usually associated with enolic compounds. It dissolves readily in alkalis, develops an intense purple coloration with ferric chloride, and yields a crystalline copper derivative when treated with copper acetate. It seems reasonable to conclude, therefore, that the anomalous behaviour of the enolic modification of camphor is due to the fact that no acidic group is combined with the atom of carbon adjoining the one to which the hydroxyl group is attached. At the same time, it is obvious that phenol and phenanthrone (Japp and Klingemann, Trans., 1893, **63**, 770) cannot owe their acidity to an acyl group; in the case of these compounds, the existence of neighbouring unsaturated linkings must be held to exert a modifying effect on their properties (compare Thiele, *Annalen*, 1899, **306**, 87).

The method which has been adopted for preparing the enolic modification of α-benzoylcamphor depends on the fact, first observed by Haller, that when sodium is dissolved in a solution of camphor in toluene, the sodium derivative of the ketone is produced. On treating this compound with benzoyl chloride, I obtained a dibenzoyl derivative which, judging by the behaviour of ethyl sodioacetoacetate under similar circumstances, might be expected to have one benzoyl group attached to carbon, whilst the other is united with oxygen.

$C_8H_{14}<\begin{matrix}C\cdot CO\cdot C_6H_5\\ ||\\ C\cdot O\cdot CO\cdot C_6H_5\end{matrix}$ 1-Benzoxy-2-benzoylcamphene.

$\begin{matrix}CO_2Et\cdot C\cdot CO\cdot C_6H_5\\ ||\\ CH_3\cdot C\cdot O\cdot CO\cdot C_6H_5\end{matrix}$ Ethyl dibenzoylacetoacetate.

This view of its constitution is supported by its behaviour on hydrolysis, as it is resolved into benzoic acid and 1-hydroxy-2-benzoylcamphene, the latter bearing the same relation to α-benzoylcamphor that ethyl hydroxycrotonate has to ethyl acetoacetate.

$C_8H_{14}<\begin{matrix}C\cdot CO\cdot C_6H_5\\ ||\\ C\cdot OH\end{matrix}$ 1-Hydroxy-2-benzoylcamphene.

$C_8H_{14}<\begin{matrix}CH\cdot CO\cdot C_6H_5\\ |\\ CO\end{matrix}$ α-Benzoylcamphor.

Several interesting points have arisen from an examination of hydroxybenzoylcamphene. In the first place, its conversion into α-benzoylcamphor is brought about quite readily by the influence of concentrated sulphuric acid, or by fusion. When the substance is dissolved in organic solvents, many specimens will slowly change spontaneously into the ketone, the alteration being stimulated by adding a small proportion of piperidine, or by exposure to sunlight. This accelerating influence of light on the isomeric change of an optically active substance was first noted in connection with ψ-nitrocamphane (Forster, Trans., 1900, 78, 253), and a similar effect has been since observed by Pope and Harvey (this vol., p. 828) in connection with the racemisation of benzylphenylallylmethylammonium iodide.

The marked enolic character of hydroxybenzoylcamphene is shown by the formation of sodium, copper, and ferric derivatives, which have been obtained in crystals; the substance combines also with phenylcarbimide, and is readily acetylated by acetic anhydride. Conversion into α-benzoylcamphor is most conveniently effected by the agency of boiling formic acid, whereby about one-half is transformed into the ketone, which, on crystallising the mixture from alcohol, separates almost entirely in the first fraction.

α-Benzoylcamphor changes very readily into the isomeride when dissolved in organic media, and fusion produces the same effect. Excepting camphor, it is the first optically active substance occurring in both forms of which a description has been placed on record, and it has been possible therefore to follow the interconversion of these two isomerides in the polarimeter. It is then found that α-benzoylcamphor, having the specific rotatory power $[\alpha]_D$ +125°, when dissolved in chloroform, gradually increases in optical activity until about 216° is reached, when no further change takes place; the hydroxy-modification, on the other hand, undergoes a diminution of specific rotatory power from $[\alpha]_D$ +281° to the maximum attained by the ketone. The point of equilibrium therefore represents the specific rotatory power of the mixed ketone and enol in a proportion of 3 : 4 approximately.

The readiness with which α-benzoylcamphor becomes transformed into the isomeride is in marked contrast with the behaviour of camphor itself. So little tendency is there on the part of the unsubstituted ketone to change into 1-hydroxycamphene, that the production of 1-benzoxy-2-benzoylcamphene is practically the first direct proof that camphor is capable of acting in the isomeric form, and hydroxycamphene itself has been isolated only by a circuitous process. This is in close agreement with the observation made by Claisen that, in ascending the series comprising triacetylmethane, diacetylbenzoylmethane, acetyldibenzoylmethane, and tribenzoylmethane, the disposition to

persist in the ketonic form increases; in other words, the more negative the character of the group replacing methylene hydrogen, the greater the tendency of the diketone to undergo enolisation.

Before proceeding to the experimental portion of this paper, it is necessary to mention that when the enolic modification of benzoylcamphor is benzoylated, the dibenzoyl derivative produced by the direct action of benzoyl chloride on sodium camphor is regenerated. This is of greater importance than may appear, at first sight, to be the case, because it was possible that the alkali used in hydrolysing the dibenzoyl compound would convert the freshly produced *α*-benzoylcamphor into an enolic substance, isomeric with 1-hydroxy-2-benzoylcamphene,

$$C_8H_{14}\begin{cases}CH\cdot CO\cdot C_6H_5\\ |\\ CO\end{cases} \longrightarrow C_8H_{14}\begin{cases}C{:}C(OH)\cdot C_6H_5\\ |\\ CO\end{cases}.$$

If this were the case, however, the original dibenzoyl derivative must have the constitution $C_8H_{14}\begin{cases}C{:}C(C_6H_5)\cdot O\cdot CO\cdot C_6H_5\\ |\\ CO\end{cases}$, and it is scarcely conceivable that such a compound could be produced by the direct action of benzoyl chloride on the sodium derivative of camphor. Moreover, a compound of the type indicated would be comparable with the dibenzoyl derivatives of 1 : 3-diketones (compare Claisen, *Annalen*, 1896, **291**, 97), for example, the benzoyl derivative of acetyldibenzoylmethane, $(C_6H_5\cdot CO)_2C{:}C(CH_3)\cdot O\cdot CO\cdot C_6H_5$; such compounds, however, when heated with aniline, are resolved into benzoic acid and an anilide which, in the case quoted, has the formula

$$(C_6H_5\cdot CO)_2C{:}C(CH_3)\cdot NH\cdot C_6H_5,$$

whereas 1-benzoxy-2-benzoylcamphene is merely hydrolysed to enolic *α*-benzoylcamphor, accompanied by benzanilide. The same effect is produced even more readily by phenylhydrazine, which is converted into the symmetrical benzoyl derivative, and concentrated sulphuric acid also resolves the dibenzoyl compound into benzoic acid and enolic *α*-benzoylcamphor, associated with a considerable proportion of the ketonic isomeride.

The investigation of 1-hydroxy-2-benzoylcamphene and its derivatives is being continued, and changes depending on its unsaturated character will be described in a subsequent communication.

I wish to express my indebtedness to Mr. W. J. Pope for kindly undertaking the crystallographic examination of the isomeric benzoylcamphors.

Experimental.

1-Benzoxy-2-benzoylcamphene, $C_{18}H_{14}<\begin{matrix}C\cdot CO\cdot C_6H_5\\ \|\\ C\cdot O\cdot CO\cdot C_6H_5\end{matrix}$.

A solution of 150 grams of camphor in 400 grams of toluene was heated with 15 grams of sodium in a reflux apparatus on the water-bath until the metal had completely dissolved. The liquid was transferred to a wide-mouthed, cylindrical specimen jar, of about 1000 c.c. capacity, and the operation having been repeated, the united solutions were allowed to remain in the stoppered vessel during 24 hours. The dark brown liquid was then decanted from the crystalline deposit, which was broken up as quickly as possible, and covered with a fresh quantity of toluene. The contents of the jar having been thoroughly cooled by immersion in melting ice, benzoyl chloride was added in small quantities at a time, care being taken to prevent the action being confined to one portion of the material. Much heat was generated at first, but subsequently it became possible to add the chloride in quantities of 10 or 15 grams. When 50 grams had been used for every 100 grams of camphor, the product, which had set to a jelly-like mass, was allowed to remain in ice during 1 hour, then mixed with its own bulk of water, and transferred to a large separating funnel, in which it was washed three times with water, and finally dried with calcium chloride. The toluene was boiled away until a thermometer in the vapour indicated 140°, when the liquid, which had the odour of benzoyl chloride and camphor, was transferred to a beaker, and heated in boiling water until the greater portion of the camphor had been removed. Half its own bulk of alcohol was then added, and the crystals which separated during the following 24 hours were filtered, washed, and recrystallised from hot alcohol. A further quantity of the substance was obtained from the dark yellow, alcoholic mother liquor of the first crop by distilling it in a current of steam until all camphor and ethyl benzoate had been removed, and then adding half its own bulk of alcohol. The total yield amounted to 8 or 10 per cent. of the camphor employed. On analysis:

0·1784 gave 0·5182 CO_2 and 0·1074 H_2O. C = 79·22 ; H = 6·69.
0·1660 „ 0·4836 CO_2 „ 0·0989 H_2O. C = 79·45 ; H = 6·62.
$C_{24}H_{24}O_3$ requires C = 80·00 ; H = 6·66 per cent.

Benzoxybenzoylcamphene is sparingly soluble in cold alcohol, and crystallises from the hot solution in transparent, highly refractive, four-sided prisms melting at 144°; it is insoluble in water, but dissolves very readily in chloroform, acetone, ethyl acetate, ether,

pyridine, or glacial acetic acid, crystallising slowly from the last-named solvent in beautiful prisms. It is moderately soluble in boiling petroleum, which deposits it in minute prisms.

A solution containing 1·0016 grams in 25 c.c. of chloroform at 22° gave α_D 15°9′ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D$ +189·7°; 0·2502 gram dissolved in 25 c.c. of absolute alcohol at 27° gave α_D 3°45′ in the same tube, corresponding to $[\alpha]_D$ +187·3°.

The substance is odourless, and is not volatile in steam; the alcoholic solution gives no coloration with ferric chloride, and is indifferent towards ammoniacal silver nitrate. It is insoluble in aqueous caustic alkalis, but dissolves readily in concentrated sulphuric acid.

A determination of the molecular weight in benzene gave the following results:

Molecular weight of $C_{24}H_{24}O_3 = 360$.

Grams of benzene.	Gram of substance.	Grams of substance in 100 grams of solvent.	Depression of freezing point.	Molecular weight deduced.
18·054	0·3170	1·7558	0·278°	316
,,	0·3940	2·1823	0·348	314
,,	0·5152	2·8536	0·452	316

Action of Aniline on Benzoxybenzoylcamphene.—On heating 3·6 grams of the dibenzoyl derivative with 1·6 grams (1½ mols.) of aniline during 4 hours in boiling water, the substance dissolved slowly, and separated unchanged when the liquid cooled. Ten grams were therefore heated with 6 grams (2 mols.) of aniline at 110—120° during 12 hours; the liquid solidified almost immediately on being withdrawn from the oven, and when quite cold the crystals were drained on porous earthenware, treated with a very small quantity of cold alcohol, again drained, and dissolved in 20 c.c. of boiling alcohol. As soon as the liquid was cold, the crystals were filtered, washed, and recrystallised from hot alcohol, which deposited lustrous plates consisting of benzanilide, and melting at 161°. The first mother liquor, on standing during several hours, deposited the characteristic crystals of 1-hydroxy-2-benzoylcamphene.

Action of Phenylhydrazine on Benzoxybenzoylcamphene.—The dibenzoyl derivative was heated with phenylhydrazine (2 mols.) in boiling water during 4 hours. The substance dissolved rapidly, and within less than an hour the liquid was filled with long, slender needles. When cold, the crystals were drained on porous earthenware, and

extracted several times with cold ether. The residue crystallised from alcohol in lustrous, flat needles, consisting of symmetrical benzoylphenylhydrazine, and the ethereal solution, on evaporation, deposited 1-hydroxy-2-benzoylcamphene.

Action of concentrated Sulphuric Acid on Benzoxybenzoylcamphene.—Fifty grams of the finely powdered dibenzoyl derivative were added to 250 c.c. of ice-cold, concentrated sulphuric acid. After an interval of 1 hour, the pale yellow solution was poured on crushed ice, which precipitated a sticky solid; this soon became crystalline, and was then filtered, washed, and treated with excess of an aqueous solution of sodium bicarbonate in order to remove benzoic acid. The undissolved portion was filtered, drained, and fused in 50 c.c. of hot alcohol, which was rapidly cooled. The product, weighing 35 grams, was recrystallised twice from small quantities of hot alcohol, and at this stage began to soften at about 80°, melted somewhat indefinitely at 85—86°, and gave $[\alpha]_D$ +222° in chloroform. On dissolving 15 grams of the material in 75 grams of hot absolute alcohol and allowing the liquid to cool in a 6-inch crystallising dish, two forms of crystals were distinguishable, clusters of colourless needles, and isolated, flattened octahedra, which were distinctly pink; these were separated mechanically, weighing 4 grams and 8 grams respectively, the deposit from the mother liquor consisting of the octahedral form exclusively.

The two modifications were then recrystallised separately from alcohol until the melting point was constant. The needles, which gave no immediate coloration with ferric chloride, melted at 87—88°. On analysis:

0·1270 gave 0·3682 CO_2 and 0·0920 H_2O. C = 79·07; H = 8·05.

A solution containing 0·6973 gram in 25 c.c. of chloroform at 21° gave α_D 7°8′ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D$ +127·9°. The octahedra, on the other hand, developed an intense purple coloration when the alcoholic solution was treated with ferric chloride, and melted at 89°. On analysis:

0·1532 gave 0·4461 CO_2 and 0·1070 H_2O. C = 79·41; H = 7·76.

$C_{17}H_{20}O_2$ requires C = 79·69; H = 7·81 per cent.

A solution containing 0·5272 gram in 25 c.c. of chloroform at 20° gave α_D 17°30′ in a 3-dcm. tube, corresponding to $[\alpha]_D$ +276·6°.

The needles and octahedra were subsequently recognised as the ketonic and enolic modifications respectively of α-benzoylcamphor.

1-*Hydroxy*-2-*benzoylcamphene* (*Enolic α-Benzoylcamphor*),

$$C_8H_{14}<\begin{matrix}C\cdot CO\cdot C_6H_5\\ \|\\ C\cdot OH\end{matrix}.$$

Fifty grams of the dibenzoyl derivative were dissolved in 500 c.c. of boiling alcohol, and heated in a reflux apparatus with 20 grams ($2\frac{1}{2}$ mols.) of caustic potash dissolved in the minimum quantity of water. After 2 hours, the alcohol was distilled off, the residue was dissolved in water, heated on the water-bath until no alcohol remained, and diluted to 1000 c.c. with water. A current of well-washed carbon dioxide was then passed through the liquid, and when no further precipitation occurred, the colourless product, which weighed 35 grams, was filtered, washed, and dried. On recrystallising the substance from 200 c.c. of absolute alcohol, a single compound was obtained in pale pink, flattened octahedra melting at 89°. The needles accompanying hydroxybenzoylcamphene when prepared by the action of concentrated sulphuric acid on the dibenzoyl compound, were, on this occasion, absent. When analysed:

0·1569 gave 0·4571 CO_2 and 0·1108 H_2O. C = 79·45; H = 7·84.
$C_{17}H_{20}O_2$ requires C = 79·69; H = 7·81 per cent.

A solution containing 1·0227 grams in 50 c.c. of chloroform at 21° gave α_D 23°0′ in a 4-dcm. tube, whence the specific rotatory power $[\alpha]_D$ +281·1°; this fell to $[\alpha]_D$ +216° during a few hours' exposure to light. A solution, prepared by dissolving 0·2939 gram in 25 c.c. of absolute alcohol at 21°, gave α_D 6°7′ in a 2-dcm. tube, corresponding to $[\alpha]_D$ +262·2°; after 3 hours' exposure to sunlight, this had fallen to $[\alpha]_D$ +208°.

Hydroxybenzoylcamphene dissolves readily in hot alcohol, and crystallises in colourless, lustrous, transparent octahedra; the first crop consists of pink crystals, the mother liquor depositing colourless ones, but no difference between them has been recognised besides a greater tendency on the part of the pink crystals, when dissolved, to change into the ketonic modification spontaneously. This change is dealt with in detail below.

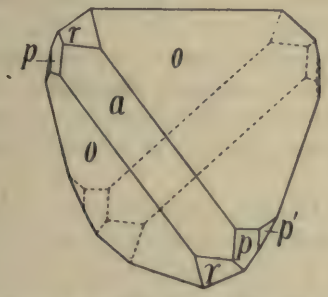
The substance is insoluble in water, but dissolves very freely in organic media. It is slowly soluble in aqueous sodium carbonate, but readily so in concentrated sulphuric acid. It is odourless, and is not volatile in steam. The alcoholic solution develops immediately an intense purple coloration with aqueous or ethereal ferric chloride.

Mr. Pope has examined the crystals of this substance, and reports as follows:

"The crystals present the habit of square plates with one pair of

opposite corners replaced, of tetrahedra with the edges replaced, or of flattened octahedra, according to the relation in size between the forms $a\{100\}$ and $o\{111\}$. These two forms are usually dominant, but occasionally the dome $r\{101\}$ is well developed; the form $p\{110\}$ is always small, and $p'\{120\}$ is only observed as a minute replacement of an edge or corner. The form $q\{011\}$ is rarely observed. The most usual habit assumed by the crystals is shown in Fig. 1. Owing to the brittle nature of the crystals, sections could not be cut for optical examination.

FIG. 1.



"Crystalline system.—Orthorhombic : Sphenoidal Hemihedrism.

$$a : b : c = 0{\cdot}9728 : 1 : 0{\cdot}6550.$$

"Forms observed: $a\{100\}$, $p\{110\}$, $p'\{120\}$, $q\{011\}$, $r\{101\}$, and $o+k\{111\}$.

"The following angular measurements were obtained :

Angle.	Number of measurements.	Limits.	Mean observed.	Calculated.
ap =100 : 110	24	43°29′— 45° 1′	44°18′	44°13′
ap' =100 : 120	38	61 57 — 63 25	62 48	—
$p'p'$ =120 : 1$\bar{2}$0	16	53 45 — 55 11	54 19	54 24
pp' =110 : 120	22	18 2 — 19 7	18 40	18 35
ao =100 : 111	43	60 4 — 61 36	60 41	60 37
oq =111 : 011	19	28 57 — 30 14	29 40	29 23
oo =111 : $\bar{1}$11	20	85 49 — 87 12	86 34	86 25
op =111 : 110	11	46 3 — 47 38	46 59	46 47½
ro =101 : 111	15	27 46 — 29 0	28 17	28 31
ar =100 : 101	47	55 18 — 56 52	56 3	—
rr =101 : $\bar{1}$01	26	67 12 — 68 27	67 56	67 54
rq =101 : 011	18	45 18 — 46 57	46 7	46 4
pr =110 : 101	19	65 48 — 67 1	66 19	66 24
pq =110 : 011	14	66 50 — 68 5	67 38	67 32
qq =011 : 0$\bar{1}$1	7	65 49 — 67 9	66 29	66 27
qq =011 : 01$\bar{1}$	12	112 40 —114 7	113 26	113 33
qo =01$\bar{1}$: 111	16	68 54 — 70 12	69 47	69 38
op' =111 : 120	9	48 46 — 50 16	49 58	49 32"

The *sodium* derivative of hydroxybenzoylcamphene was prepared by adding 0·5 gram of sodium dissolved in alcohol to a solution of 2·5 grams of the substance in cold alcohol, and allowing the pale yellow liquid to remain in the desiccator. After an interval of a few days, the crystals, which were of moderate size but somewhat indefinite in structure, were washed with alcohol and dried in the desiccator. On analysis:

0·2208 gave 0·0590 Na_2SO_4. Na = 8·65.

$C_{17}H_{19}O_2Na$ requires Na = 8·27 per cent.

The compound is readily soluble in alcohol and in water, which forms a strongly alkaline solution, dissociating when boiled. A solution containing 0·5787 gram in 25 c.c. of absolute alcohol gave α_D 13°20′ in a 3-dcm. tube, whence the specific rotatory power $[\alpha]_D$ +192·0°; this value points to almost complete dissociation having occurred, for in that case the substance would give $[\alpha]_D$ +190·5°, assuming that transformation into the equilibrium mixture immediately followed dissociation.

The *copper* derivative, obtained by adding 1·8 grams ($\frac{1}{2}$ mol.) of copper acetate dissolved in the minimum quantity of boiling alcohol to a solution containing 5·1 grams of hydroxybenzoylcamphene in 20 c.c. of absolute alcohol, crystallises in lustrous, sage-green needles.

0·1895 gave 0·0248 CuO. Cu = 10·46.

$(C_{17}H_{19}O_2)_2Cu$ requires Cu = 11·07 per cent.

The substance is insoluble in water, even on boiling, but dissolves sparingly in petroleum; it is very readily soluble in benzene, chloroform, or nitrobenzene, forming brownish-green solutions. Acetone, which dissolves it very readily, yields a pure green solution, which also results from dissolving it in ethyl or methyl alcohol; the last-named solvent dissolves it but sparingly, even when boiled, depositing it in minute, green needles as the liquid cools. It is moderately soluble in ether, which yields a green solution.

The *ferric* derivative was formed on adding to a solution of 2·5 grams of the hydroxy-compound in ether 0·5 gram ($\frac{1}{3}$ mol.) of ferric chloride dissolved in alcohol, followed by 0·8 gram (1 mol.) of sodium acetate in water. The liquid which remained after two days' exposure to air was decanted, and the crystals were drained on porous earthenware, and washed several times with water, and finally with dilute alcohol. The product has the colour of potassium permanganate.

0·1961 gave 0·0171 Fe_2O_3. Fe = 6·10.

$(C_{17}H_{19}O_2)_3Fe$ requires Fe = 6·82 per cent.

The substance is quite insoluble in water, but dissolves freely in petroleum, chloroform, ether, alcohol, acetone, or nitrobenzene, forming solutions having the colour of port.

Effect of Heat on Hydroxybenzoylcamphene.—A specimen of hydroxybenzoylcamphene giving $[\alpha]_D$ +281° in chloroform was heated at the temperature of boiling water during 4 hours. The substance solidified on cooling, and then gave $[\alpha]_D$ +267° in the same solvent. It therefore changes into the equilibrium mixture less rapidly than the ketonic modification.

Action of concentrated Sulphuric Acid on Hydroxybenzoylcamphene.—Single crystals of the hydroxy-compound giving $[\alpha]_D$ +281° were powdered and dissolved in 4 parts of concentrated sulphuric acid. After 48 hours, the solution was poured on crushed ice, and the sticky precipitate, when crystalline, was filtered, washed, and recrystallised from alcohol; this deposited crystals among which both modifications could be recognised easily. The mixture gave $[\alpha]_D$ +211° in chloroform.

Regeneration of the Dibenzoyl Derivative from Hydroxybenzoylcamphene.—Three grams of the hydroxy-compound were dissolved in 3 grams (3 mols.) of pyridine in a wide-mouthed stoppered bottle, and cooled by immersion in melting ice; 2·8 grams (2 mols.) of benzoyl chloride were then added drop by drop. After 3 days, the semi-solid product was treated with ether, filtered, and washed with ether. On evaporating the filtrate and distilling off the pyridine, the residue, consisting of the impure dibenzoyl derivative, became crystalline on cooling. The yield, including 0·5 gram obtained on dissolving out the pyridine hydrochloride with water, amounted to 3·5 grams.

α-Benzoylcamphor, $C_8H_{14}\begin{cases}CH\cdot CO\cdot C_6H_5\\ |\\ CO\end{cases}$.

Ten grams of 1-hydroxy-2-benzoylcamphene were heated in a reflux apparatus with 40 grams of boiling formic acid (sp. gr. 1·2) during 4 hours. The liquid was poured into a large volume of cold water, which precipitated a colourless oil; this solidified almost immediately when scratched with a glass rod, and was then filtered, washed, and dissolved quickly in 30 c.c. of absolute alcohol. This solution was immersed in cold water, and, after half an hour, filtered as rapidly as possible, because the filtrate began to deposit a mixture of both modifications when agitated. The needles obtained in this way consisted solely of the ketonic form, and amounted to 4·5 grams. Recrystallised from alcohol, they formed colourless prisms melting at 87—88°, and gave no immediate coloration with ferric chloride. On analysis:

0·1645 gave 0·4792 CO_2 and 0·1144 H_2O. C = 79·45; H = 7·72.

$C_{17}H_{20}O_2$ requires C = 79·69; H = 7·81 per cent.

A solution containing 0·5 gram dissolved in 25 c.c. of chloroform at 21° gave α_D 5°0′ in a 2-dcm. tube if examined without any delay, whence the specific rotatory power $[\alpha]_D$ +125·0°; 0·25 gram dis-

solved in 25 c.c. of absolute alcohol at 21° gave α_D 2°45′ in the same tube, corresponding to $[\alpha]_D$ +137·5°.

The substance is moderately soluble in methyl or ethyl alcohol, and dissolves very freely in benzene, ether, acetone, or chloroform; it is only moderately soluble in boiling petroleum, which dissolves the enolic modification very readily. An alcoholic solution gives no immediate coloration with ferric chloride.

The crystals of this substance have been examined by Mr. Pope, who reports as follows:

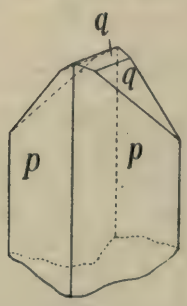
"The crystals are long, colourless, transparent needles of calcite-like lustre. The predominant form is the prism $p\{110\}$, and the crystals are elongated in the direction of the c-axis; the dome $q\{011\}$ is small, and the form $q'\{012\}$ occurs as a minute replacement of the edge $011 : 0\bar{1}1$ (Fig. 2). The crystals are very brittle, and the optic axial plane is $c(001)$. In the absence of pyramid forms or characteristic etch-figures, it is impossible to say whether the crystals are or are not sphenoidally hemihedral.

"Crystalline system.—Orthorhombic.

$$a : b : c = 0{\cdot}7375 : 1 : 1{\cdot}0224.$$

"Forms observed: $p\{110\}$, $q\{011\}$, $q'\{012\}$.

Fig. 2.



"The following angular measurements were obtained:

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
$pp = 110 : \bar{1}10$	15	106°32′—107°56′	107°18′	107°11′
$pp = 110 : 1\bar{1}0$	19	72 4 — 73 52	72 49	—
$pq = 110 : 011$	14	64 7 — 65 28	64 45	64 54
$pq = 110 : 0\bar{1}1$	7	114 42—115 50	115 21	115 6
$qq = 011 : 0\bar{1}1$	23	90 34 — 92 2	91 16	—
$q'q' = 012 : 0\bar{1}2$	18	53 25 — 54 47	54 5	54 9
$qq' = 011 : 012$	7	18 1 — 18 59	18 34	18 35½"

Effect of Heat on α-Benzoylcamphor.—A specimen giving $[\alpha]_D$ +128° in chloroform was heated at the temperature of boiling water during 4 hours. The product remained superfused, but solidified rapidly when sown with a single crystal of the original substance. A determination of the specific rotatory power in chloroform gave $[\alpha]_D$ +231°, and on allowing the solution to evaporate spontaneously, and recrystallising the residue from a small quantity of alcohol, the first crop of crystals consisted exclusively of the enolic form.

Interconversion of the Isomeric Benzoylcamphors.

Reference has been made to the fact that certain specimens of 1-hydroxy-2-benzoylcamphene, when dissolved in chloroform, spontaneously undergo diminution in rotatory power, owing to gradual conversion into the ketonic isomeride. If the change is allowed to proceed, a point of equilibrium is reached when the specific rotatory power of the mixture is about $[\alpha]_D$ +216°. The interval which elapses before the rotatory power becomes constant is, in the case of a 2 per cent. solution, about 6 days, the curve associating rotation with time being hyperbolic. On exposing a freshly prepared solution to sunlight, the rapidity of the change becomes greatly exaggerated, the position of equilibrium being reached in 2 or 3 hours. These remarks do not apply to the colourless crystals of hydroxybenzoylcamphene, a solution in chloroform having been preserved in darkness during 12 hours, exposed to bright sunlight during 2 hours, and even sown with a crystal of the ketonic isomeride, without suffering any perceptible reduction in optical activity. It appears, therefore, that some exciting agent is required to initiate the change, but it is noteworthy that the ketone, so far as can be ascertained, is more sensitive in this respect than the isomeride.

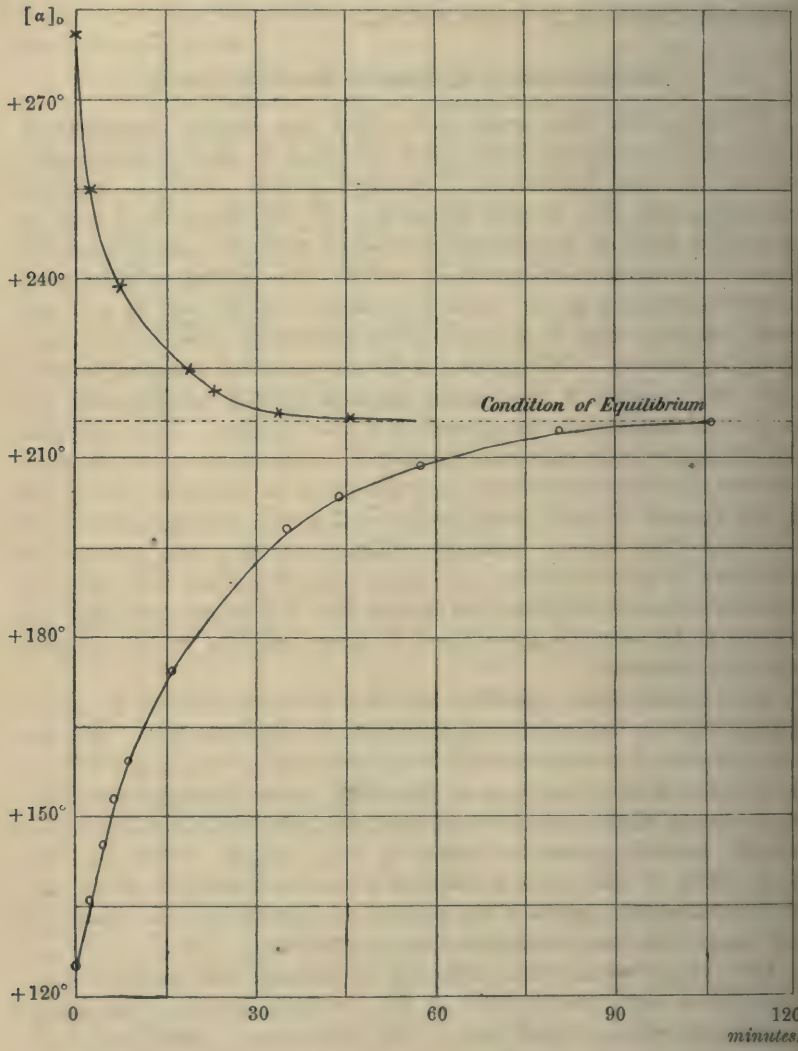
As in former cases, piperidine has been observed to exert a stimulating effect on the interconversion of the two modifications. A 2 per cent. solution of the colourless hydroxy-compound, giving $[\alpha]_D$ +280·4°, was treated with 0·2 per cent. of piperidine; after three-quarters of an hour, during which period the solution was protected from light, the specific rotatory power had fallen to $[\alpha]_D$ +220°. Advantage has been taken of this action to compare the rates of speed at which the two modifications approach the position of equilibrium, the result of the comparison being represented in the curve on p. 1000.

From this it appears that, although the change from ketone to enol takes place more readily than in the converse direction, the latter modification, when started, reaches the position of equilibrium much more rapidly than the ketone.

Action of Ferric Chloride on the Isomeric Benzoylcamphors.

As already stated, the enolic modification of α-benzoylcamphor, unlike the enolic modification of camphor itself, develops immediately

Interconversion of the two isomerides in a chloroform solution containing 0·05 per cent. of piperidine.



an intense purple coloration with ferric chloride dissolved in water or in ether. This is due to the formation of the ferric derivative,

$(C_{17}H_{19}O_2)_3Fe$, but it is highly probable that in absence of sodium acetate, such derivatives as $C_{17}H_{19}O_2FeCl_2$ and $(C_{17}H_{19}O_2)_2FeCl$ are produced at the same time, because the first-named compound has been isolated, and its solutions in organic solvents are found to be wine red, lacking the blue shade which the purple coloration exhibits. Moreover, when a very dilute solution of the enolic derivative in alcohol is treated with a single drop of a moderately concentrated aqueous solution of ferric chloride, a blue coloration is developed, and can be changed to the characteristic wine red shade of dissolved $(C_{17}H_{19}O_2)_3Fe$ by adding aqueous sodium acetate (compare W. Wislicenus, *Annalen*, 1896, **291**, 173).

The production of the purple coloration has been observed when ethereal ferric chloride is added to the enolic modification dissolved in benzene, ether, acetone, chloroform, methyl alcohol, or ethyl alcohol; it is also developed when aqueous ferric chloride is added to an alcoholic solution of the substance, but a solution in chloroform remains colourless.

The ketonic modification, dissolved in methyl or ethyl alcohol, gives no immediate coloration with an aqueous solution of ferric chloride, but in a few seconds the yellow solution deepens in colour, becoming greenish-brown, and then very deep green; finally, after an interval of many minutes, the liquid acquires the purple tinge developed by the enolic modification. The same remarks apply when ethereal ferric chloride is employed, the changes in this case being more rapid. Solutions in acetone and ether give the green coloration almost immediately with ethereal ferric chloride, and quickly reach the bluish-violet stage. When chloroform or benzene is employed to dissolve the ketone, ferric chloride in ether produces an immediate green coloration, which rapidly becomes bluish-violet. In the case of benzene and ether, the final coloration is exactly the same as that developed by the enolic modification itself.

Phenylurethane Derivative of 1-*Hydroxy*-2-*benzoylcamphene*,

$$C_8H_{14}\begin{cases}C\cdot CO\cdot C_6H_5\\ \|\\ C\cdot O\cdot CO\cdot NH\cdot C_6H_5\end{cases}.$$

The union of hydroxybenzoylcamphene with phenylcarbimide takes place very slowly. Five grams of the finely powdered hydroxy-compound were placed in a stoppered weighing bottle, and covered with 3 grams of phenylcarbimide. After an interval of 7 days, during which the vessel was kept in a desiccator, the contents had changed to a hard, crystalline cake, which, when drained on porous earthenware, weighed 6 grams. As an alcoholic solution still developed an intense coloration with ferric chloride, the product was heated on the

water-bath with a small quantity of alcohol, cooled, filtered, and washed with cold alcohol until the washings remained indifferent to an ethereal solution of ferric chloride. The residue was then dissolved in 50 grams of boiling alcohol, which deposited minute, transparent crystals melting at 117°.

0·1264 gave 0·3568 CO_2 and 0·0785 H_2O. C = 76·98; H = 6·90.
$C_{24}H_{25}O_3N$ requires C = 76·80; H = 6·66 per cent.

A solution containing 0·4913 gram in 25 c.c. of chloroform at 21° gave α_D 7°30′ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D^-$ +190·8°.

The phenylurethane derivative is moderately soluble in alcohol and ether, dissolving very freely in chloroform. Alcoholic solutions are indifferent towards aqueous and ethereal ferric chloride.

1-*Acetoxy*-2-*benzoylcamphene*, $C_8H_{14}\begin{cases}C\cdot CO\cdot C_6H_5\\ \|\\ C\cdot O\cdot CO\cdot CH_3\end{cases}$.

Fifteen grams of 1-hydroxy-2-benzoylcamphene were heated in a reflux apparatus with 50 grams of boiling acetic anhydride during 3 hours. On pouring the liquid into a considerable volume of cold water, the derivative began to crystallise before the anhydride was nearly decomposed, and after an interval, was collected, washed, and recrystallised twice from alcohol. It separates from that solvent in long, lustrous, rectangular plates, and melts at 107°.

0·1760 gave 0·4912 CO_2 and 0·1170 H_2O. C = 76·12; H = 7·39.
$C_{19}H_{22}O_3$ requires C = 76·51; H = 7·38 per cent.

A solution containing 0·5003 gram in 25 c.c. of chloroform at 21°, gave α_D 7°45′ in a 2-dcm. tube, whence the specific rotatory power $[\alpha]_D$ +193·6°; 0·2522 gram dissolved in 25 c.c. of absolute alcohol at 21° gave α_D 3°48′ in the same tube, corresponding to $[\alpha]_D$ +188·3°.

The substance dissolves freely in hot alcohol, but is only moderately soluble in the cold medium. It is also readily soluble in chloroform, ethyl acetate, glacial acetic acid, or boiling petroleum, separating from the last-named solvent in the characteristic rectangular plates.

In its behaviour towards concentrated sulphuric acid, acetoxybenzoylcamphene resembles the corresponding benzoxy-derivative; it dissolves in the agent without rise of temperature, becoming converted into a mixture of the two benzoylcamphors, in which the enolic modification preponderates.

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CVI.—*Studies in the Camphane Series. Part V. Halogen Derivatives of* p-*Cymene from substituted Nitrocamphanes.*

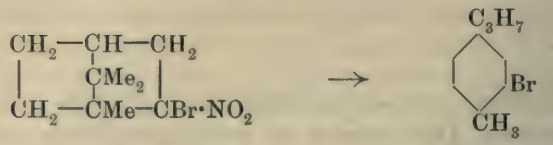
By Martin Onslow Forster and William Robertson, A.R.C.S.

It has been mentioned that when 1 : 1-bromonitrocamphane is dissolved in concentrated sulphuric acid, the anhydride, $C_{10}H_{14}ONBr$, is always accompanied by a viscous oil having a fragrant odour (Forster, Trans., 1899, **75**, 1145). Although the yield of this material does not exceed 10 per cent. of the halogen compound employed, an investigation of the anhydride and its derivatives has placed at our disposal a quantity sufficient for systematic examination; this has been undertaken, therefore, in the hope that identification might afford some explanation of the obscure change taking place when 1 : 1-bromonitrocamphane is converted into the anhydride.

Suspecting that the oil, which contains bromine, might arise from some impurity in the crude bromonitrocamphane, we ascertained that it is also produced when the material is recrystallised from acetic acid previous to dissolution in sulphuric acid. Moreover, a similar compound, containing chlorine in place of bromine, attends the conversion of 1 : 1-chloronitrocamphane into the anhydride, and consequently that substance has been included in the investigation. From this, we have ascertained that the oils in question are halogen derivatives of *p*-cymene, in which substitution has occurred in the ortho-position relatively to the methyl group.

This result is noteworthy in being the second established instance of the production of substituted cymenes from camphor derivatives of known constitution. The transformation of camphor itself into cymene has been the subject of numerous investigations, but the first record of the observation of this change in derivatives of camphor occurs in a paper by Marsh and Hartridge (Trans., 1898, **73**, 852), who found that on preparing carvenone by the action of concentrated sulphuric acid on 1 : 1-dichlorocamphane, the product is contaminated with a small proportion of a chloro-derivative, which they believed to be chlorocymene [Me : Cl : Pr^{β} = 1 : 2 : 4]; the formation of this compound is not recorded by Bredt (*Annalen*, 1901, **314**, 369), who repeated the experiments of Marsh and Hartridge.

It will be noticed that the position of the halogen atom as regards the methyl and *iso*propyl groups is in complete agreement with the requirements of Bredt's formula for camphor, assuming no alteration to have taken place in the attachment of the bromine or chlorine.



1 : 1-Bromonitrocamphane. Bromo-*p*-cymene.

It is scarcely possible, however, to furnish an explanation of the change so simple as that given by Bredt (*loc. cit.*) for the conversion of camphor into cymene. Most likely the nitro-group plays an important part in the reaction, as the liberation of nitrous fumes has been observed during the production of the substance. In this connection, it is noteworthy that 1-nitrocamphane does not yield cymene when dissolved in cold concentrated sulphuric acid, and appears to be quite indifferent towards that agent.

Bromocymene [$CH_3 : Br : C_3H_7^{\beta} = 1 : 2 : 4$] *from* 1 : 1-*Bromonitrocamphane.*

The accumulated bye-product from 500 grams of bromonitrocamphane was washed several times with concentrated sulphuric acid, treated with water and dilute sodium carbonate, extracted with ether, dried with calcium chloride, and freed from ether, which deposited 50 grams of a pale brown, somewhat viscous oil, having a powerful, fragrant odour. We have not succeeded in isolating from this product a pure specimen of bromocymene, but there is every probability that the latter forms the chief constituent of the mixture. The following evidence, coupled with the fact that 1 : 1-chloronitrocamphane yields chlorocymene under similar conditions, led to this conclusion.

After the separation described above, the oil was distilled in steam, which separated it from a less volatile, resinous material. At this stage, it was optically active, giving α_D − 13°31′ in a 2-dcm. tube, and contained 33·3 per cent. of bromine; the substance was saturated, and did not contain nitrogen. It was then agitated with concentrated sulphuric acid, and after remaining in contact with that agent during some days was washed with sodium carbonate and distilled in an atmosphere of steam. The pale yellow oil decomposed when distilled under atmospheric pressure, evolving hydrogen bromide and becoming charred. It was, therefore, distilled under 26 mm. pressure, the major portion boiling at 128—130°, and then redistilled under the same reduced pressure, the final product boiling at 129—130°; although a mobile, colourless oil, the substance became pale yellow on exposure to sunlight. On analysis:

0·1614 gave 0·3230 CO_2 and 0·0888 H_2O. C = 54·58; H = 6·12.
0·2188 ,, 0·4361 CO_2 ,, 0·1216 H_2O. C = 54·35; H = 6·17.
0·2509 ,, 0·2120 AgBr. Br = 35·95.

$C_{10}H_{13}Br$ requires C = 56·34; H = 6·10; Br = 37·56 per cent.

From these results, it appears that the bromocymene was still contaminated with some oxygenated impurity, which is optically active, because the material analysed gave α_D $-4°48'$ in a 2-dcm. tube. Such a substance could only arise by condensation of 2 mols. of bromonitrocamphane taking place according to the equation

$$2C_{10}H_{16}O_2NBr - 2H_2O - N_2O = C_{20}H_{28}OBr_2;$$

a compound having this empirical formula would contain 54·0, 6·3, and 36·0 per cent. of carbon, hydrogen, and bromine respectively. These requirements were so nearly met by our analyses, that a determination of the molecular weight of the substance in benzene was made.

Molecular weight of $C_{10}H_{13}Br$, 213; $C_{20}H_{28}OBr_2$, 444.

Grams of benzene.	Grams of substance.	Grams of substance in 100 grams of benzene.	Depression of the freezing point.	Molecular weight deduced.
17·70	0·7082	4·0011	0·938°	213·3
19·59	0·1467	0·7488	0·182	215·4

This result pointed unquestionably to the substance being bromocymene, and was borne out by a determination of the density, which gave 1·257 at 16°, the value recorded by Landolph being 1·269 at 17·5°.

As it seemed likely that the oxygenated compound of the type indicated would be decomposed by alcoholic soda, the substance was submitted to this treatment, because it is known that bromocymene is indifferent towards the agent in question. The resulting substance was almost colourless, and boiled at 229°, the temperature at which bromocymene distils. On analysis:

0·1836 gave 0·1588 AgBr. Br = 36·82.

$C_{10}H_{13}Br$ requires Br = 37·56 per cent.

With the object of proving that this compound is derived from *p*-cymene, an attempt was made to reduce it in alcohol with sodium. Forty grams were dissolved in 300 c.c. of absolute alcohol, and heated in a reflux apparatus with 40 grams of sodium, which was added in small quantities at a time, and soon gave rise to the separation of sodium bromide. When the metal had dissolved, water was added, and a current of steam was passed through the liquid until the alcohol had completely separated. On diluting the distillate with water, a colourless oil was precipitated, and this was collected, dried with

calcium chloride, and distilled; it boiled at 172° (uncorr.) under 770 mm. pressure. On analysis:

0·1226 gave 0·3990 CO_2 and 0·1147 H_2O. C = 88·76; H = 10·40.
$C_{10}H_{14}$ requires C = 89·54; H = 10·45 per cent.

The identity of the hydrocarbon was placed beyond doubt by the operation recommended for this purpose by Widman; oxidation with potassium permanganate in presence of caustic soda gave rise to a specimen of hydroxy*iso*propylbenzoic acid melting at 157°.

Anhydride of Chloronitrocamphane, $C_{10}H_{14}ONCl$.

In preparing the anhydride of chloronitrocamphane, it is of greater importance to keep the rise of temperature under control than even in the case of the corresponding bromo-derivative. One hundred grams of chloronitrocamphane were added in small quantities to 800 c.c. of concentrated sulphuric acid, cooled below 0° by a freezing mixture, and at no time was the temperature of the liquid allowed to rise above 5°. The acid soon became dark brown, and a colourless, fragrant oil was produced, whilst towards the end of the operation hydrogen chloride was liberated. When all the chloronitrocamphane had been added, the liquid was allowed to remain in a separating funnel until the oil had risen to the surface, the acid being then run slowly on to crushed ice; this precipitated a yellow solid, which was washed, drained on earthenware, and recrystallised twice from boiling alcohol. The yield under favourable circumstances amounts to 25 per cent. On analysis:

0·2345 gave 14·8 c.c. of nitrogen at 20° and 773 mm. N = 7·35.
0·2094 „ 0·1521 AgCl. Cl = 17·97.
$C_{10}H_{14}ONCl$ requires N = 7·02; Cl = 17·79 per cent.

The anhydride dissolves readily in hot alcohol, from which it crystallises in aggregates of opaque prisms; the melting point is not very definite, but the substance darkens above 200°, and melts at about 230° to a deep brown liquid which evolves gas. It is readily soluble in cold benzene and in ethyl acetate, crystallising from the latter in minute octahedra; boiling water dissolves the compound very sparingly, but it is moderately soluble in boiling petroleum.

Chlorocymene [$CH_3 : Cl : C_3H_7^{\beta} = 1 : 2 : 4$] *from* 1 : 1-*Chloronitrocamphane.*

The oil referred to in describing the preparation of the anhydride of chloronitrocamphane was decolorised by treatment with concentrated sulphuric acid, and washed with water, followed by sodium carbonate; after being distilled in a current of steam, the product was collected

with ether, dried with calcium chloride, and distilled, 26 grams being obtained from 300 grams of chloronitrocamphane.

The substance obtained in this way was a colourless, mobile liquid boiling at 211—212° (uncorr.) under 768 mm. pressure; it had a sp. gr. 1·0122 at 16°, and although in these respects it agreed closely with *p*-chlorocymene, the fact that it gave α_D −0°35′ in a 2-dcm. tube indicates that the substance was not quite pure. On analysis:

0·1651 gave 0·4250 CO_2 and 0·1136 H_2O. C = 70·20; H = 7·64.
0·2198 „ 0·1863 AgCl. Cl = 20·92.
$C_{10}H_{13}Cl$ requires C = 71·26; H = 7·72; Cl = 21·02 per cent.

A determination of the molecular weight in benzene gave the following result:

Molecular weight of $C_{10}H_{13}Cl$, 168·5.

Grams of benzene.	Grams of substance.	Grams of substance in 100 grams of benzene.	Depression of the freezing point.	Molecular weight deduced.
25·03	0·1358	0·5425	0·178°	152·4
„	0·2988	1·1938	0·380	157·1

Conversion of Chloronitrocamphane Anhydride into the Isomeride.

Chloronitrocamphane anhydride was dissolved in 5 parts of alcohol and heated in a reflux apparatus with 2 parts of concentrated hydrochloric acid during half an hour. The liquid was poured into cold water, and the precipitate crystallised from dilute alcohol, which deposits it in needles. On analysis:

0·2038 gave 13·0 c.c. of nitrogen at 16° and 754 mm. N = 7·38.
0·1500 „ 0·1065 AgCl. Cl = 17·56.
$C_{10}H_{14}ONCl$ requires N = 7·02; Cl = 17·79 per cent.

The substance is readily soluble in alcohol and is best recrystallised from boiling petroleum, in which it is only sparingly soluble; it crystallises from the latter in transparent, six-sided plates, and melts at 248°.

The *benzoyl* derivative, prepared by the Schotten-Baumann method, crystallises from alcohol in lustrous white leaflets, and melts at 166°.

0·1546 gave 0·0712 AgCl. Cl = 11·39.
$C_{17}H_{18}O_2NCl$ requires Cl = 11·69 per cent.

Action of Hydroxylamine on the Anhydride of Chloronitrocamphane.

Ten grams of chloronitrocamphane anhydride were dissolved in 50 c.c. of absolute alcohol, to which was added 8 grams of dry sodium carbonate. The mixture was then heated during 5 hours in a reflux apparatus with 10 grams of hydroxylamine hydrochloride dissolved in the minimum quantity of water. Alcohol was then distilled off on the water-bath, and the residue treated with a considerable quantity of water, filtered, and washed. The compound was recrystallised from alcohol, which deposited transparent, rectangular plates.

0·2951 gave 0·1805 AgCl. Cl = 15·13.
0·2634 „ 0·1625 AgCl. Cl = 15·25.
$C_{10}H_{17}O_2N_2Cl$ requires Cl = 15·27 per cent.

The hydroxylamino-derivative of chloronitrocamphane anhydride melts at 187°, when it turns brown and evolves gas. It reduces ammoniacal silver nitrate readily on warming.

The *benzoyl* derivative dissolves somewhat sparingly in alcohol, from which it crystallises in lustrous, white needles, and melts at 164°. The alcoholic solution is indifferent towards ammoniacal silver nitrate.

Action of Nitric Acid on the Anhydrides of Bromonitrocamphane and Chloronitrocamphane.

When the anhydride of bromonitrocamphane, obtained by dissolving that substance in concentrated sulphuric acid, is treated with cold fuming nitric acid, it is dissolved immediately, and gas is liberated, but the diluted liquid does not yield a definite product. If, however, the isomeric anhydride is treated in the same way, no change takes place, and the substance merely dissolves, but on heating the liquid a nitro-derivative is obtained.

Ten grams of the isomeric anhydride were consequently heated with 40 c.c. of fuming nitric acid of sp. gr. 1·52 during several minutes, the liquid, when cold, being poured into a considerable volume of water, which precipitated a colourless oil. This solidified rapidly, and was then collected, washed, and crystallised from hot alcohol. On analysis:

0·2911 gave 25·1 c.c. of nitrogen at 17° and 763 mm. N = 10·23.
0·3084 „ 0·1997 AgBr. Br = 27·56.
$C_{10}O_{13}O_3N_2Br$ requires N = 9·69; Br = 27·68 per cent.

The substance therefore appears to be a nitro-derivative. It crystallises from alcohol in rosettes of transparent prisms melting at 103°, and is insoluble in sodium carbonate or caustic alkali. Unlike the substance from which it is derived, it gives Liebermann's reaction for

nitroso-derivatives. Hot caustic soda decomposes it slowly, giving rise to infracampholenonitrile.

The same difference in behaviour towards nitric acid is exhibited by the anhydrides of 1 : 1-chloronitrocamphane.

Twenty-five grams of the isomeride melting at 248° were heated with 100 c.c. of fuming nitric acid during one minute only, the solution being poured on crushed ice; the oil which separated soon solidified, and was crystallised from alcohol, which deposited flat prisms resembling the corresponding bromo-derivative, and melting at 71—72°.

0·2204 gave 0·1309 AgCl. Cl = 14·68.

$C_{10}H_{13}O_3N_2Cl$ requires Cl = 14·52 per cent.

The substance dissolves very readily in hot alcohol, and in cold benzene, ethyl acetate, or glacial acetic acid; it is moderately soluble in boiling petroleum, from which it crystallises on cooling, and is also slightly soluble in boiling water. Decomposition with hot caustic soda is effected more readily than in the case of the corresponding bromo-derivative, infracampholenonitrile being produced. It gives Liebermann's reaction for nitroso-derivatives and does not reduce an ammoniacal solution of silver nitrate; it is distinguished from the original anhydride by indifference towards benzoyl chloride, which does not yield a derivative.

Behaviour of the Nitro-compound on Reduction.—Ten grams of the nitro-derivative obtained from the isomeric anhydride of 1 : 1-chloronitrocamphane were dissolved in 50 c.c. of glacial acetic acid, and treated with 20 grams of zinc dust. The metal was added in small quantities at a time, and the liquid was cooled after each treatment, but in spite of these precautions nitrous gases were liberated on each occasion. When all the zinc had been added, the product was allowed to remain at the ordinary temperature during 12 hours, then heated on the water-bath during 2 hours, and finally filtered. On diluting the acetic acid with water, a white, crystalline precipitate was obtained; this weighed nearly 8 grams, and was readily identified as the anhydride melting at 248°. The filtrate from this compound was rendered alkaline with caustic soda, and distilled in a current of steam, which carried over a small quantity of infracampholenonitrile; the distillate was tested for hydrazine, but no reduction of ammoniacal silver nitrate occurred.

From this experiment it appears probable that the nitro-groups in the derivatives of the anhydrides are attached to nitrogen.

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CVII.—*Reduction of aγ-Dibenzoylpropane and Dibenzoyldiphenylbutadiene.*

By FRANCIS R. JAPP, F.R.S., and ARTHUR C. MICHIE, B.Sc.

JOHANNES WISLICENUS has published, conjointly with some of his pupils (*Annalen*, 1898, **302**, 191—244), a series of papers under the collective title, "Formation of Carbocyclic Compounds by the Conversion of 1 : 5- and 1 : 6-Diketones into their Pinacones." Portions of the investigation treat of matters which have already been dealt with by other methods in papers on the condensations of benzil with ketones published by one of us in conjunction with various collaborators; but of the latter work, unfortunately everything except the first paper—"On Additive and Condensation Compounds of Diketones with Ketones" (Japp and Miller, Trans., 1885, **47**, 11; also *Ber.*, 1885, **18**, 179)—has escaped the notice of the German investigators. The consequence is that they occasionally describe, as new, facts already known; that they fail to compare their compounds with others previously described, even where this is of importance; and that they sometimes misinterpret their results. We have therefore subjected certain portions of their work to a careful revision.

J. Wislicenus and C. K. Kuhn (*loc. cit.*, p. 215) describe the preparation of $a\gamma$-dibenzoylpropane; its reduction, by the action of sodium on an ethereal solution of the substance floating on water, to an uncrystallisable oil which they regard as the cyclic pinacone 1 : 2-diphenyl-1 : 2-dihydroxy*cyclo*pentane, the reaction taking place according to the equation

$$\begin{matrix} C_6H_5\cdot CO\cdot CH_2 \\ C_6H_5\cdot CO\cdot CH_2 \end{matrix}\!\!>\!CH_2 + 2H = \begin{matrix} C_6H_5\cdot C(OH)\cdot CH_2 \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{matrix}\!\!>\!CH_2;$$

and, finally, the reduction of the latter compound by hydriodic acid to a substance which they regard as 1 : 2-diphenyl*cyclo*pentane, $\begin{matrix} C_6H_5\cdot CH\cdot CH_2 \\ C_6H_5\cdot CH\cdot CH_2 \end{matrix}\!\!>\!CH_2$, a white, granular, crystalline mass melting at 108°.

These authors are apparently unaware that a substance claiming to be a 1 : 2-diphenyl*cyclo*pentane (m. p. 47°) has already been prepared. Japp and Burton (Trans., 1887, **51**, 423), who obtained it by the reduction of anhydracetonebenzil (*diphenyl*cyclo*pentenolone*), $\begin{matrix} C_6H_5\cdot C{=\!=\!=}CH \\ C_6H_5\cdot C(CH)\cdot CH_2 \end{matrix}\!\!>\!CO$, were uncertain whether it was a 1 : 1-phenylbenzyl*cyclo*butane or a 1 : 2-diphenyl*cyclo*pentane, as the constitution of anhydracetonebenzil itself was not then settled. Japp and Lander

(Trans., 1897, 71, 128 and 131) conclusively showed that it had the latter constitution. Later on, we will briefly recapitulate their arguments, adding a further experimental proof.

Our first impression was that the hydrocarbons melting at 47° and 108° respectively might be the *cis-* (meso) and the *trans-* (racemic) form. We therefore resolved to prepare the hydrocarbon melting at 108° by Wislicenus and Kuhn's method: in the first place, in order to compare the two compounds, and, secondly, to ascertain whether the hydrocarbon melting at 47° was formed at the same time, as, in the method of purification adopted by these authors, it might possibly have been overlooked.

We first prepared $\alpha\gamma$-dibenzoylpropane and, incidentally, greatly improved the yield of this substance by hydrolysing the dibenzoylglutaric ester with dilute sulphuric acid instead of with caustic alkali. The "acid hydrolysis" of the ketonic ester observed by Wislicenus and Kuhn was thus entirely avoided, and only "ketonic hydrolysis" occurred.

We then reduced the $\alpha\gamma$-dibenzoylpropane as prescribed by Wislicenus and Kuhn, and obtained the "pale-yellow oil" which they could not induce to crystallise, and which they therefore analysed after leaving it in a vacuum desiccator until the weight was constant. They obtained figures agreeing with those required for the expected cyclic pinacone, 1 : 2-diphenyl-1 : 2-dihydroxy*cyclo*pentane.

We find, however, that, by appropriate treatment, no fewer than five distinct substances can be separated from this "pale-yellow oil": (1) the above cyclic pinacone (m. p. 103—104·5°); (2) in small quantity, $\alpha\epsilon$-diphenyl-$\alpha\epsilon$-dihydroxypentane,

$$C_6H_5\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot C_6H_5$$

(m. p. 84—88°), which we were afterwards able to prepare in somewhat larger quantity by reducing $\alpha\gamma$-dibenzoylpropane with sodium in boiling alcohol; (3) a small quantity of unchanged $\alpha\gamma$-dibenzoylpropane, which is always present, even when the sodium in Wislicenus and Kuhn's method is used in the enormous excess of more than 20 times the theoretical amount; (4) a colourless oil, soluble in light petroleum, and (5) a yellow resin insoluble in light petroleum. That the "pale-yellow oil" gave, in Wislicenus and Kuhn's hands, figures agreeing with those required for the pinacone, was therefore a pure coincidence.

We found that the pinacone could be obtained much more readily, and in a state of purity, by reducing $\alpha\gamma$-dibenzoylpropane in hot aqueous alcoholic solution with aluminium amalgam.

Chromium trioxide, in acetic acid solution, readily reconverts the pinacone into $\alpha\gamma$-dibenzoylpropane.

As regards the hydrocarbon, we prepared it both according to

Wislicenus and Kuhn's directions from the "pale-yellow oil," and afterwards from the pure pinacone. By their method of purification, one and the same substance, agreeing fairly well with their description, was isolated in both cases. It is of very indefinite character and is certainly not a diphenyl*cyclo*pentane. Thus it does not boil even at 340° under 12 mm. pressure, whereas 1 : 2-diphenyl*cyclo*pentane from anhydracetonebenzil boils quite constantly at 189° under 12 mm. pressure. Again, it must appear somewhat strange that Wislicenus and Kuhn's diphenyl*cyclo*pentane should melt as high as 108° and be practically insoluble in alcohol, seeing that Wislicenus and Carpenter's tetraphenyl*cyclo*pentane (*Annalen*, 1898, **302**, 229), in spite of its two additional phenyl groups, melts as low as 81° and is soluble in alcohol.

We have therefore no hesitation in saying that Wislicenus and Kuhn's supposed 1 : 2-diphenyl*cyclo*pentane is a highly polymerised substance, and that the action of hydriodic acid on the pinacone is much less simple than these authors have assumed. Indeed, the known action of acids upon pinacones, in producing dehydration and migration, might have suggested the need for caution on this point.

As it was apparently impossible to obtain 1 : 2-diphenyl*cyclo*pentane from the pinacone, it was of interest to ascertain whether the reverse change could be effected; whether the known 1 : 2-diphenyl*cyclo*pentane (m. p. 47°) from anhydracetonebenzil could be oxidised either to a pinacone—identical or stereoisomeric with that above described—or, failing this, to *αγ*-dibenzoylpropane. We found that the latter transformation readily takes place when the hydrocarbon is treated with chromium trioxide in acetic acid solution in the cold:

$$\begin{matrix} C_6H_5\cdot CH\cdot CH_2 \\ | \\ C_6H_5\cdot CH\cdot CH_2 \end{matrix}\!\!>\!CH_2 \;+\; 3O \;=\; \begin{matrix} C_6H_5\cdot CO\cdot CH_2 \\ | \\ C_6H_5\cdot CO\cdot CH_2 \end{matrix}\!\!>\!CH_2 \;+\; H_2O.$$

1 : 2-Diphenyl*cyclo*pentane (m. p. 47°). *αγ*-Dibenzoylpropane.

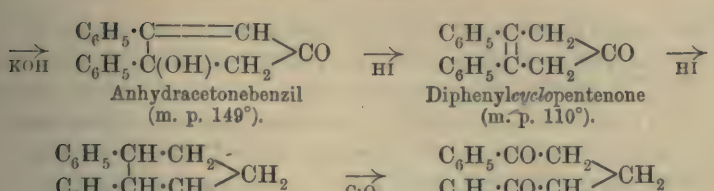
All attempts to obtain an intermediate oxidation product proved fruitless.

The foregoing reaction entirely confirms the constitution of a 1 : 2-diphenyl*cyclo*pentane which Japp and Lander assigned to the hydrocarbon $C_{17}H_{18}$ (m. p. 47°) from anhydracetonebenzil.

Before leaving this part of the subject, we will arrange in their order the different compounds which have been obtained by one of us, conjointly with pupils, in the transformation of benzil and acetone, on the one hand, into *αγ*-dibenzoylpropane, on the other:

$$\underbrace{\begin{matrix} C_6H_5\cdot CO \\ | \\ C_6H_5\cdot CO \end{matrix} \;+\; \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>\!CO}_{} \xrightarrow{KOH} \begin{matrix} C_6H_5\cdot CO \\ | \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{matrix}\!\!>\!CO \qquad \begin{matrix} CH_3 \\ \\ \end{matrix}$$

Acetonebenzil (m. p. 78°).



The constitution of anhydracetonebenzil has been proved by a study of its reactions, too long to recapitulate here (compare Japp and Lander, Trans., 1897, **71**, 123); that of diphenyl*cyclo*pentenone by its formation from anhydracetonebenzil, by its giving a phenylhydrazone, and by its being oxidised quantitatively to diphenylmaleic acid by sodium hypobromite (*ibid.*, 132); and finally, that of 1 : 2-diphenyl-*cyclo*pentane both by its formation from diphenyl*cyclo*pentenone by reduction, and by its conversion into αγ-dibenzoylpropane by oxidation, as also by the fact that it behaves as a saturated compound, both towards bromine and towards hydriodic acid at 150° (Trans., 1887, **51**, 424).*

Wislicenus and Lehmann (*Annalen*, 1898, **302**, 195) have studied the action of alcoholic sodium hydroxide and sodium ethoxide on a mixture of benzil and acetophenone. By the first method they obtained αβ-dibenzoylphenylethylene (αβ-dibenzoylcinnamene, anhydracetophenonebenzil),† $\begin{matrix} C_6H_5\cdot C{:}CH\cdot CO\cdot C_6H_5 \\ C_6H_5\cdot CO \end{matrix}$, which they recognised as identical with the compound obtained by Japp and Miller by the action of warm aqueous potash on a mixture of benzil and acetophenone (Trans., 1885, **47**, 35). Wislicenus and Lehmann's method, however, yields

* It is not often that Dr. M. M. Richter, the author of the invaluable *Lexikon der Kohlenstoff-Verbindungen*, ventures to combine his already sufficiently arduous task of compilation with that of criticism. With regard to the present question, however, after accepting Wislicenus and Kuhn's compound at their own valuation as "1,2-Diphenyl-R-Pentamethylen, Sm. 108°," he indicates his scepticism regarding the 1 : 2-diphenyl*cyclo*pentane of m. p. 47° by querying its constitution. Again, Richter-Anschütz's *Organische Chemie* (9th edition, **2**, 10) gives only Wislicenus and Kuhn's compound.

The reasons for this preferential treatment of the non-existent 1 : 2-diphenyl*cyclo*pentane are assuredly not *chemical*.

† I must, I think, decline the responsibility for some, at least, of the changes of name that this compound has undergone. The first systematic name assigned to it by Dr. Klingemann and myself was "αβ-dibenzoylstyrolene," and under this name it was described in the Proceedings (1889, **5**, 136). On our sending the full paper to the Journal, Mr. C. E. Groves, at that time Editor, pointed out to us that the official name for "styrolene" was "cinnamene," and that, in any case, the compound would be thus indexed. We therefore made the required change to "αβ-dibenzoylcinnamene" (compare Trans., 1890, **57**, 662); but I now find that the compound appears in the Collective Index as "αβ-dibenzoylstyrene."—F. R. J.

the compound mixed with dibenzoyldiphenylbutadiene, and is therefore inferior to that described by Japp and Klingemann (Trans., 1890, 57, 673), in which, by employing as a condensing agent alcoholic potassium hydroxide very slightly diluted with water, pure $a\beta$-dibenzoylphenylethylene is obtained. Wislicenus and Lehmann have overlooked the latter paper, with the result that, in addition to employing the foregoing unsuitable method of preparation, they make various determinations without indicating that these are merely confirmations of some already made: thus an ebullioscopic determination of the molecular weight, already determined cryoscopically by Japp and Klingemann (*ibid.*, 674), and a few indications of the crystalline form (two angles measured), whereas Tutton (Trans., 1890, 57, 714) gives full crystallographical measurements of $a\beta$-dibenzoylphenylethylene and ten of its derivatives. If this were all, the matter would not, of course, be worth calling attention to. But this want of acquaintance with the foregoing work causes the German authors to go somewhat astray in their interpretation of the chief reaction of their paper—the reduction of dibenzoyldiphenylbutadiene.

Dibenzoyldiphenylbutadiene, which had not been previously prepared, was obtained by Wislicenus and Lehmann (*loc. cit.*, 198) by the condensation of 1 molecular proportion of benzil with 2 of acetophenone under the influence of alcoholic sodium ethoxide. They leave it an open question whether the compound has the symmetrical or the unsymmetrical constitution:

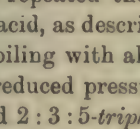
$$\begin{array}{l} C_6H_5C{:}CH\cdot CO\cdot C_6H_5 \\ C_6H_5C{:}CH\cdot CO\cdot C_6H_5 \end{array} \quad \text{or} \quad \begin{array}{l} C_6H_5\cdot C{:}CH\cdot C\cdot C_6H_5 \\ C_6H_5\cdot CO \quad\quad CH\cdot CO\cdot C_6H_5 \end{array}.$$

They subjected this compound to the action of various reducing agents, and obtained various products. One of the latter, which was formed by reducing the substance with hydriodic acid in glacial acetic acid solution and boiling the resinous product with alcoholic potassium hydroxide, and to which the formula $C_{20}H_{14}O$ is assigned, attracted our attention; partly because it was difficult to see how it could have such a formula, and partly because it was obviously identical with an already known compound of a different formula. The authors describe the substance as crystallising from alcohol in "long, colourless, flat needles, melting at 92—94°." They found benzoic acid in the alkaline solution from the treatment of the resin, and explain the formation of the compound as follows: "By the action of the alkali, the resinous reduction product of the diketone—the latter a compound containing four phenyl groups—has been broken up into a molecule of benzoic acid and a compound, $C_{20}H_{14}O$, containing three phenyl groups."

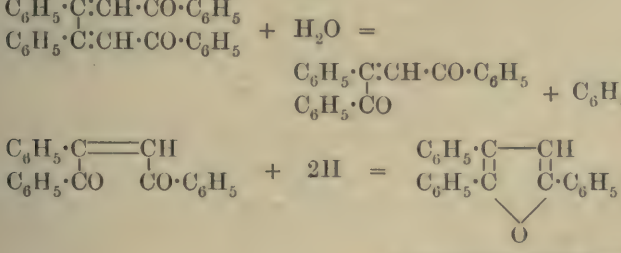
Leaving difficulties with the hydrogen out of the question, three phenyl groups would account for C_{18}, leaving C_2 over for the grouping

of these three phenyl groups, and the authors refrain from hazarding any explanation as to how a dibenzoyldiphenylbutadiene, whether symmetrical or unsymmetrical, could yield a compound in which three phenyl groups are attached to the group C_2.

Speculation on this point is, however, unnecessary, inasmuch as the compound has not the formula $C_{20}H_{14}O$, but $C_{22}H_{16}O$ (Wislicenus and Kuhn's figures agree, on the whole, rather better with this formula than with that which they calculate), and is identical with the substance which Japp and Burton (Trans., 1887, **51**, 430) obtained by the reduction of $a\beta$-dibenzoylphenylethylene with hydriodic acid. The latter authors describe the compound as forming "colourless, long, flat prisms melting constantly at 92—93°," which agrees with Wislicenus and Lehmann's description. Japp and Klingemann (*Ber.*, 1888, **21**, 2933; Trans., 1890, **57**, 663) showed later that the compound was 2 : 3 : 5-*triphenylfurfuran*,



We therefore repeated the reduction of dibenzoyldiphenylbutadiene with hydriodic acid, as described by Wislicenus and Lehmann, omitting, however, the boiling with alcoholic potash, and, instead, distilling the product under reduced pressure. We thus obtained without difficulty *acetophenone* and 2 : 3 : 5-*triphenylfurfuran*, the formation of the former of which explains that of the latter. In the first stage of the reaction, the dibenzoyldiphenylbutadiene parts with one $C_6H_5{\cdot}CO{\cdot}CH$ group by hydrolysis as acetophenone, and the resulting $a\beta$-dibenzoylphenylethylene is then reduced to triphenylfurfuran. Assuming, for simplicity, the symmetrical formula for dibenzoyldiphenylbutadiene, the process may be represented as follows:



2 : 3 : 5-Triphenylfurfuran (m. p. 92—93°).

The boiling with alcoholic potash employed by Wislicenus and Lehmann, has therefore nothing to do with the formation of the triphenylfurfuran, although this treatment may, of course, have aided in removing impurities.

The various facts above referred to, which have escaped Wislicenus and Lehmann's notice, are to be found collected together in *Beilstein*, 3, p. 308, in the article "Dibenzoylstyrol."

Experimental.

Preparation of Ethyl Dibenzoylglutarate (*Ethyl Methylenedibenzoylacetate*), $C_6H_5\cdot CO\cdot CH(CO_2C_2H_5)\cdot CH_2\cdot CH(CO_2\cdot C_2H_5)\cdot CO\cdot C_6H_5$.—This substance was prepared by the condensation of formaldehyde with ethyl benzoylacetate as described by Knoevenagel (*Annalen*, 1894, 281, 57), except that we employed as a condensing agent piperidine instead of diethylamine.* One hundred and twenty grams of ethyl benzoylacetate and 24 grams of a 40 per cent. aqueous solution of formaldehyde were mixed, and 15 grams of piperidine gradually added, cooling with water all the time. As soon as the liquid began to thicken, alcohol was added; this prevented the whole from setting to a hard cake, as in Knoevenagel's experiment. The compound is deposited from the solution in a crystalline condition, and after recrystallisation from alcohol, forms colourless needles melting constantly at 92·5°, showing straight extinction in polarised light and giving no coloration with ferric chloride. (Knoevenagel gives the melting point as 86°, but he employed only 2 grams of ethyl benzoylacetate in the preparation of the substance, and the quantity obtained was probably insufficient for complete purification. He does not indicate the crystalline form.)

The yield varied somewhat. The most favourable result was 100 grams of once crystallised product from the foregoing quantities.

Wislicenus and Kuhn (*Annalen*, 1898, 302, 215) prepared ethyl dibenzoylglutarate by the action of methylene diiodide on ethyl benzoylsodioacetate. In this way, they obtained it as an uncrystallisable oil, which gave a cherry-red coloration with ferric chloride.† In one experiment, they obtained an isomeric ethyl dibenzoylglutarate melting at 130·5°.

Preparation of $a\gamma$-*Dibenzoylpropane*, $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot C_6H_5$.—Wislicenus and Kuhn prepared this compound by boiling the "crude, oily ethyl dibenzoylglutarate" with a 10 per cent. aqueous solution of potassium hydroxide for 9 hours. This process, however, yielded, along with the diketone, γ-benzoylbutyric acid. In order to

* This was done merely because we happened to have a stock of the former base. In many of these condensations, Knoevenagel uses either base indifferently.

† This coloration may, of course, have been due to an enolic form of ethyl dibenzoylglutarate. Still, some proof of the absence of unchanged ethyl benzoylacetate from the uncrystallisable oil would appear desirable.

avoid this "acid hydrolysis," we hydrolysed the ester by boiling it with dilute sulphuric acid.

Forty grams of crystallised ethyl dibenzoylglutarate were boiled for 2 hours with 200 c.c. of a mixture of equal volumes of concentrated sulphuric acid and water, using a reflux condenser. A more dilute acid does not produce hydrolysis, whilst one more concentrated completely resinifies the substance; indeed, even with an acid of the foregoing strength there is a certain amount of resinification, the organic substance, which floats in a fused condition on the surface of the liquid, being reddish-brown at the end of the process, whilst the aqueous layer is highly fluorescent. The evolution of carbon dioxide is practically complete at the end of the 2 hours, and longer boiling diminishes the yield. The flask was cooled with water, shaking all the time, and the product, which was thus obtained in a granular form, was separated, washed with water, dissolved in ether, and the ethereal solution was shaken with sodium carbonate solution, dried with calcium chloride, and concentrated. The dibenzoylpropane was deposited in lustrous laminæ, a second crystallisation sufficing to furnish a colourless product melting at 67·5°, as described by Wislicenns and Kuhn. From alcohol, it crystallises in blades; from light petroleum, in which it is only sparingly soluble, in very slender needles. The yield was 65 per cent. of the theoretical.

Reduction of Dibenzoylpropane in Ethereal solution with Sodium.—The process of reduction was carried out exactly as prescribed by Wislicenus and Kuhn (*loc. cit.*, 221). An ethereal solution of 10 grams of dibenzoylpropane was introduced into a flask along with water, and 40 grams of sodium in small pieces was gradually added, cooling all the time. (Wislicenus and Kuhn merely state that a very large excess of sodium is to be employed, without specifying the amount.) The addition of the sodium took about 2 days. The ethereal solution was separated from the yellow, aqueous layer, dried with anhydrous sodium sulphate, and evaporated to expel the ether, after which it was left in a vacuum desiccator over sulphuric acid for several days. It formed a pale yellow syrup, agreeing with the description given by Wislicenus and Kuhn, who analysed it in this condition.

As our final results in dealing with this substance differ very materially from those of Wislicenus and Kuhn, we venture to describe the method of purification more fully than would otherwise be necessary.

The syrupy substance was extracted with successive portions of boiling light petroleum ("ligroin"), using a reflux condenser; it became crystalline on warming with the light petroleum, but the crystals afterwards melted again. After four extractions there remained only a hard, yellow resin, insoluble in light petroleum. The four extracts,

which were kept separate, deposited on cooling a colourless oil, which on standing partly crystallised in short, *thickish* needles, which give a *red* coloration with concentrated sulphuric acid. The first extract yielded most crystals. The united mother liquors from these crops gave on concentration tufts of *very slender* needles, totally distinct from the others. After recrystallisation from light petroleum they melted at 84—88°, and when free from the thickish needles gave only a *yellow* coloration with sulphuric acid. They proved to be *aε-diphenyl-aε-dihydroxypentane* described later on. The last mother liquor gave a small quantity of unaltered dibenzoylpropane.

The purification of the substance crystallising in thickish needles was a matter of some difficulty owing to the oil with which they were contaminated. In the case of the first crop some fairly pure substance was obtained by recrystallising from a mixture of benzene and light petroleum. The other portions were dissolved in boiling light petroleum, and the flask containing the decanted hot solution shaken under the tap until a portion of the oil had separated; the solution, again decanted from the oil, gave the short, thickish, prismatic needles. The various portions of crystalline substance obtained by these various methods were finally united and recrystallised from light petroleum until they showed the constant melting point of 103—104·5°. In polarised light, the needles show oblique extinction. They dissolve in concentrated sulphuric acid, giving a deep red, strongly fluorescent solution. Owing to loss in purification, the yield of pure substance was only 1·4 grams.

Occasionally in the crystallisation of the foregoing substance the tufts of slender needles (m. p. 84—88°) made their appearance. These could be got rid of by pouring off the solution from the thickish needles before the others separated.

After both kinds of crystals had been as far as possible removed, there remained a colourless oil which could not be made to crystallise by contact with any of the three crystalline substances isolated from the mixture. It was not further examined.

Analysis of the substance melting at 103—104·5° gave figures agreeing with those required by the cyclic pinacone, 1 : 2-*diphenyl*-1 : 2-*dihydroxy*cyclo*pentane*,

$$\begin{matrix} C_6H_5\cdot C(OH)\cdot CH_2 \\ | \qquad\qquad \diagdown \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{matrix} > CH_2.$$

0·1652 gave 0·4846 CO_2 and 0·1059 H_2O. C = 80·00; H = 7·12.

$C_{17}H_{18}O_2$ requires C = 80·31; H = 7·08 per cent.

Afterwards, when we had prepared the cyclic pinacone in quantity by the reduction of dibenzoylpropane with aluminium amalgam, we found that it was deposited from glacial acetic acid in crystals of the

formula $C_{17}H_{18}O_2,C_2H_4O_2$ sparingly soluble in the cold acid. The pinacone should be dissolved in the glacial acetic acid with the aid of a gentle warmth, as heating with the acid turns it yellow, and decomposes it. In the form of this double compound the pinacone can, as the following experiment shows, be readily separated from the other substances formed in Wislicenus and Kuhn's process of reduction.

Ten grams of dibenzoylpropane in ethereal solution were again reduced with sodium as already described, but instead of treating the syrupy product with light petroleum, it was dissolved in a little more than its own bulk of glacial acetic acid. As it showed no tendency to crystallise, a small portion was removed and frozen with ice and salt; on allowing it to thaw, crystals of the double compound remained, and with these the crystallisation of the rest was started. The substance was deposited in large crystals; after expelling the acetic acid of crystallisation, the pinacone thus obtained weighed 3·7 grams, and, save for a very faint brownish tinge, was pure. After a second crystallisation from acetic acid, it was colourless. The crystals effloresce only very slowly at the ordinary temperature. For analysis, they were dried by pressing between filter paper and then exposing to the air for two and a half hours.

0·8735 lost, on heating at 70°, 0·1688. $C_2H_4O_2 = 19·32$.

$C_{17}H_{18}O_2,C_2H_4O_2$ requires $C_2H_4O_2 = 19·10$ per cent.

The acetic acid mother liquor, separated from the first crop of crystals of the foregoing double compound and containing the remainder of the reduction product, yielded, by spontaneous evaporation, only a small quantity of the same crystals, imbedded, however, in a thick syrup which showed no tendency to crystallise. We estimate that the crude, syrupy reduction compound, analysed as the cyclic pinacone by Wislicenus and Kuhn, contains not more than 50 per cent. of that substance.

Reduction of Dibenzoylpropane with Sodium in boiling Alcohol.—Twenty grams of dibenzoylpropane were dissolved in absolute alcohol and 24 grams of sodium gradually added to the boiling solution. On diluting with water, an oil separated; this was taken up with ether, the ethereal solution dried with fused potassium carbonate, and the ether expelled on the water-bath. The yellow, oily product showed no tendency to crystallise, but by the following rather tedious process we succeeded in isolating a crystalline substance from it. The oil was dissolved in a moderate bulk of alcohol; the solution was diluted with an equal volume of water, shaken in a corked flask, and allowed to stand. As soon as the oil had settled, the solution, which was still somewhat turbid, was decanted into a beaker and again allowed to

stand, so as to allow part of the alcohol to evaporate. More oil separated, and the liquid, which had become clear, was again decanted and allowed to evaporate in a vacuum desiccator over sulphuric acid, when it deposited clear, prismatic crystals.* The oils were redissolved in alcohol and again treated in the same way, repeating the process as often as crystals were obtained. The united crops of crystals were recrystallised, once from dilute alcohol by the same method, and then twice from light petroleum. From the latter solvent, the substance was deposited in very slender needles melting at 84—88°, identical with those obtained in small quantity along with 1 : 2-diphenyl-1 : 2-dihydroxy*cyclo*pentane in the treatment of Wislicenus and Kuhn's reduction product with light petroleum. In the present case, if the crystallisation was allowed to go on too long, a slight separation of the thickish, short needles of the cyclic pinacone from the light petroleum solution was observed, but by filtering as soon as the slender needles were deposited, the pinacone remained in the mother liquor.

The new compound crystallises from dilute alcohol in lustrous, slender, six-sided prisms, from light petroleum in very slender needles, both showing straight extinction in polarised light. The melting point is not sharp; the substance fuses between 84—88° to a turbid liquid which clears at 92°. If free from the cyclic pinacone, it gives only a yellow coloration with concentrated sulphuric acid.

Analysis gave figures agreeing with the formula of *$a\epsilon$-diphenyl-$a\epsilon$-dihydroxypentane*, $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}C_6H_5$.

0·1314 gave 0·3817 CO_2 and 0·0926 H_2O. C = 79·22; H = 7·83.
0·1356 „ 0·3953 CO_2 „ 0·0951 H_2O. C = 79·50; H = 7·79.
$C_{17}H_{20}O_2$ requires C = 79·69; H = 7·81 per cent.

The yield of pure substance from 20 grams of dibenzoylpropane was only 0·3 gram.

Reduction of Dibenzoylpropane by Aluminium Amalgam.—This reaction furnishes the best means of obtaining 1 : 2-diphenyl-1 : 2-dihydroxy*cyclo*pentane, but the success of the method depends on the observance of certain precautions. No reduction takes place in absolute alcohol; the best result was obtained with a solution in alcohol diluted with half its volume of water. The condition of the amalgam is important; if it is allowed to heat up and oxidise during its preparation, it becomes inert. The following method gave a good result.

Ten grams of aluminium powder, previously freed from oil by treatment with ether in a Soxhlet's extractor, was shaken for a few seconds with 10 c.c. of a saturated alcoholic solution of mercuric chloride

* Sometimes an oil separates at this point also, and does not crystallise until after long standing. Once crystals have been obtained, it is better to start the crystallisation with nuclei of these.

which had been diluted with 100 c.c. of the same solvent, was then rapidly filtered through a disc of loose felt on a perforated porcelain funnel, using the filter pump, washed quickly with alcohol, and at once transferred to a flask containing 10 grams of dibenzoylpropane, 200 c.c. of alcohol, and 100 c.c. of water. The flask was fitted with a condensing tube and was heated on a metal plate over the water-bath, repeating the heating every day for some time. At first the liquid deposited, on cooling overnight, blades of dibenzoylpropane, the quantity of which, however, daily diminished, until at last they ceased to appear. The reduction must, however, be carried considerably beyond this point. After a week, as the evolution of hydrogen had become very slow, a second portion of 10 grams of aluminium amalgam was added, and a third was sometimes found necessary at the end of another week. From a fortnight to three weeks' heating was thus required according to the activity of the amalgam, and it was found that the addition of the latter in successive portions, as just described, gave a better result than when it was added all at once. The filtered and concentrated solution ought to yield, on diluting slightly with water, needles of the cyclic pinacone, unmixed with the blades and laminæ of unaltered dibenzoylpropane. If, however, the latter substance is present, the mixture of crystals should be dissolved in a little glacial acetic acid with the aid of a gentle warmth; the liquid on standing deposits crystals of the cyclic pinacone containing acetic acid of crystallisation, whilst the dibenzoylpropane remains in solution. If it is necessary to concentrate this solution, it should be done under diminished pressure, in order to avoid the decomposing action of the hot acid on the pinacone.

If the reduction has been properly carried out, the yield is quantitative.

The pinacone was deposited from dilute alcohol in thick needles. For analysis, it was recrystallised from light petroleum, from which it separated in short needles melting at 103—104·5°, identical with the compound of the same melting point obtained by the reduction of dibenzoylpropane with sodium in ethereal solution. Analysis gave figures agreeing with those required by 1 : 2-*diphenyl*-1 : 2-*dihydroxy*-cyclo*pentane*.

0·1816 gave 0·5340 CO_2 and 0·1190 H_2O. C = 80·19; H = 7·28.
0·1511 „ 0·4440 CO_2 „ 0·0965 H_2O. C = 80·13; H = 7·09.
$C_{17}H_{18}O_2$ requires C = 80·31; H = 7·08.

Stereoisomerides were not observed.

Oxidation of 1 : 2-*Dibenzoyl*-1 : 2-*diphenyl*cyclo*pentane to* αγ-*Dibenzoylpropane.*—1·5 grams of the cyclic pinacone were dissolved in glacial acetic acid with the aid of a gentle warmth, and the same weight of

chromium trioxide, dissolved in the same menstruum, was gradually added. As no oxidation had taken place after standing for 20 hours in the cold, the mixture was warmed for a short time on the water-bath and then poured into water. Laminæ of *αγ-dibenzoylpropane* separated. After freeing from acid by means of sodium carbonate, an ethereal solution deposited crystals showing the melting point of αγ-dibenzoylpropane (67·5°) and indistinguishable from that substance.

Reduction of 1 : 2-*Dibenzoyl*-1 : 2-*diphenyl*cyclo*pentane with Hydriodic Acid and Red Phosphorus.*—This reduction was carried out exactly as described by Wislicenus and Kuhn, heating the cyclic pinacone with hydriodic acid and red phosphorus in sealed tubes at 150—160°. One set of experiments was performed with the crude syrupy pinacone, as prescribed by these authors. Afterwards we used the pure pinacone. Finally we tried the experiment, not mentioned by Wislicenus and Kuhn, of boiling *dibenzoylpropane* with hydriodic acid (sp. gr. 1·7) and red phosphorus for 13 hours.

In every case, by employing the method of purification prescribed by these authors—namely, of repeatedly dissolving the product of reduction in ether and precipitating it with alcohol—we obtained what appeared to be the same substance. It was a white, wax-like solid, which showed a tendency to become more granular by repeated precipitation and which finally melted at 105—108°. It was readily soluble in ether and in benzene, practically insoluble in alcohol. In these respects it agreed fairly well with the description of Wislicenus and Kuhn's hydrocarbon melting at 108°.

We introduced a portion of this product (prepared from the syrupy pinacone) into a bulb which was exhausted by means of a filter-pump and then heated in a spermaceti-bath, the temperature being gradually raised to 340°. At that temperature and under a pressure of 12 mm., there was a mere trace of a distillate, but the greater part of the substance showed no sign of volatilising. The distillate did not crystallise.

We had intended to make an ebullioscopic determination of the molecular weight of the substance, but after the result of the foregoing experiment, we did not regard this as necessary. The molecular weight was obviously very much higher than that of a diphenyl*cyclo*pentane—the substance which Wislicenus and Kuhn had supposed it to be.

The mother liquors obtained in the purification of the foregoing substance were examined. By evaporating to dryness and distilling the residue under diminished pressure a crystalline substance was obtained, but in quantity too small for further examination. It was not identical with Japp and Burton's 1 : 2-diphenyl*cyclo*pentane (m. p. 47°). The latter compound is not formed in this reduction.

Boiling point of 1 : 2-*Diphenyl*cyclo*pentane* (m. p. 47°) *from Anhydr*-*acetonebenzil.*—Japp and Burton (Trans., 1887, **51**, 423) found that, under atmospheric pressure, this hydrocarbon boils, with partial decomposition, at 305°. In order better to compare it with Wislicenus and Kuhn's supposed 1 : 2-diphenyl*cyclo*pentane, we determined its boiling point under reduced pressure. A well-crystallised specimen melting at 47° was employed for the purpose. It passed over without decomposition quite constantly at 189° under 12 mm. pressure (temperature of oil-bath 200°). The colourless distillate solidified to a mass of white crystals of unchanged substance.

Oxidation of 1 : 2-*Diphenyl*cyclo*pentane* (m. p. 47°).—0·6 gram of 1 : 2-diphenyl*cyclo*pentane (m. p. 47°) was dissolved in glacial acetic acid, a solution of 1·2 grams of chromium trioxide in acetic acid was gradually added, the mixture was allowed to stand for 20 hours, and poured into water. Solid caustic soda was added so as to leave the liquid slightly acid, after which the solution was extracted with ether. The ethereal solution, after removing acids, deposited laminæ of *αγ-dibenzoylpropane*, which after recrystallisation showed the correct melting point of 67·5°. A supersaturated solution of the substance in alcohol at once crystallised on seeding it with a crystal of dibenzoylpropane.

Benzoic acid was also formed, together with a small quantity of an acid crystallising from water in minute prisms or needles melting at 133·5°, which we were unable to identify.

Reduction of Diphenyldibenzoylbutadiene.—Five grams of diphenyldibenzoylbutadiene were boiled with 200 grams of glacial acetic acid, 10 grams of hydriodic acid (sp. gr. 1·7), and 2 grams of red phosphorus for 3½ hours, employing a reflux condenser. The liquid was filtered, precipitated with water, and extracted with ether; the ethereal solution was treated with sulphurous acid and sodium carbonate, dried with calcium chloride, and after expelling the ether, the residue was distilled under a pressure of 12 mm. Part passed over at 80—85°; it smelt of acetophenone, and when cooled in melting ice and touched with a small crystal of acetophenone, solidified. Nearly the whole of the residue distilled when the oil-bath was at 275—295°. It was dissolved in alcohol. On cooling, an oil separated. The mother liquor was evaporated to a small bulk and crystallisation was started by seeding with 2 : 3 : 5-triphenylfurfuran. The oils were repeatedly boiled up with alcohol and the clear solutions obtained on cooling were treated in the same manner. In this way, a relatively good yield of colourless needles was obtained. After recrystallisation they melted at 92—93°, were indistinguishable from crystals of 2 : 3 : 5-triphenylfurfuran (m. p. 92—93°) and, like these, showed straight extinction in polarised light. Wislicenus and Lehmann obtained in the analysis

of this substance: C = 88·85, H = 5·60 (mean of two analyses), the formula of triphenylfurfuran, $C_{22}H_{16}O$, requiring C = 89·19, H = 5·40. The formula $C_{20}H_{14}O$, calculated by Wislicenus and Lehmann, requires C = 88·88, H = 5·20, so that analysis alone is hardly competent to decide between the two formulæ. The proof of the correctness of the formula $C_{22}H_{16}O$ is to be found in the fact that the same compound is formed in a quantitative yield by the reduction of *aβ*-dibenzoylphenylethylene and by other methods which leave no doubt as to its constitution. The above experiment shows, moreover, that the treatment of the product of the reduction of diphenyldibenzoylbutadiene with alcoholic potash, which Wislicenus and Lehmann regarded as essential to the formation of the substance melting at 92—23°, was unnecessary.

The chief products of the reduction of diphenyldibenzoylbutadiene in our experiment were, therefore, *acetophenone*, formed by hydrolysis, and 2 : 3 : 5-*triphenylfurfuran*, formed by the reduction of *aβ*-dibenzoylphenylethylene, the other product of hydrolysis (see Introduction).

The other compounds obtained by Wislicenus and Lehmann may have been present in the residue, sparingly soluble in alcohol, which remained after the extraction of the triphenylfurfuran; but we did not examine this further.

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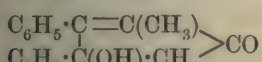
CVIII.—*Homologues of Anhydracetonebenzil.*

By FRANCIS R. JAPP, F.R.S., and ANDREW N. MELDRUM, B.Sc.

ANHYDRACETONEBENZIL, one of the products of the condensation of benzil with acetone under the influence of potassium hydroxide, was shown by Japp and Lander (Trans., 1897, 71, 123) to be a *diphenylcyclopentenolone* of the formula $\begin{matrix} C_6H_5\cdot C \!=\!\!=\!\!= CH \\ | \qquad\quad \diagdown \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{matrix}\!\!>\!CO$.

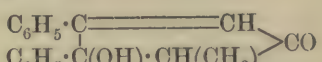
By the condensation of benzil with homologues of acetone of the general formulæ $CH_2R'\cdot CO\cdot CH_3$ and $CH_2R'\cdot CO\cdot CH_2R'$, Japp and Burton (Trans., 1887, 51, 431) prepared various homologues of anhydracetonebenzil. The constitution of those members of this class which are formed from symmetrical homologues of acetone follows, as a matter of course, from that of anhydracetonebenzil itself; thus the condensation product of benzil with diethyl ketone (*loc. cit.*, p. 432) is *aβ-dimethylanhydracetonebenzil*, $\begin{matrix} C_6H_5\cdot C \!=\!\!=\!\!= C(CH_3) \\ | \qquad\quad \diagdown \\ C_6H_5\cdot C(OH)\cdot CH(CH_3) \end{matrix}\!\!>\!CO$ (m. p.

150°), if we distinguish the CH group in the pentacarbon ring of anhydracetonebenzil as the α-, and the CH_2 group as the β-position (compare Trans., 1899, **75**, 1019). But in the case of the compounds obtained from unsymmetrical homologues of acetone, there are two possibilities; thus, from benzil and methyl ethyl ketone both the α- and the β-methyl derivative may be obtained:



α-Methylanhydracetonebenzil (m. p. 118°).

and



β-Methylanhydracetonebenzil (m. p. 180·5°).

Japp and Lander (*loc. cit.*, p. 129) found that α-derivatives are more stable towards permanganate in the cold than β-derivatives, and in this way arrived at the conclusion that the monoalkyl derivatives of anhydracetonebenzil obtained by Japp and Burton belonged to the β-class.* This conclusion was confirmed by Japp and Findlay, who found that these compounds did not interact with benzaldehyde to yield benzylidene derivatives, whereas anhydracetonebenzil compounds containing the methylene group readily do so.

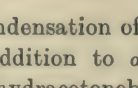
We have now repeated and largely extended Japp and Burton's work.

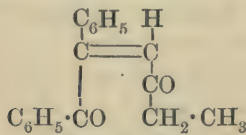
Their method of preparing these compounds (*loc. cit.*, p. 431) consisted in warming a mixture of the ketone in question—thus methyl ethyl ketone—and benzil with aqueous potassium hydroxide for some days at a temperature of 20—25°. This procedure left unchanged a considerable amount of benzil, which had to be removed by washing the product with ether. We find that in this way a soluble isomeride was removed along with the benzil, and overlooked. By using a slight excess of the ketone and heating to a somewhat higher temperature, we ensure the total conversion of the benzil. The separation of the two isomerides then presents no difficulty.

In the foregoing mode of preparation, the sparingly soluble isomeride generally predominates; but we find that, by allowing the condensation of the ketone with benzil to take place at the ordinary temperature in a 0·5 per cent. solution of potassium hydroxide in absolute alcohol, the more soluble isomeride is generally formed in greater quantity.

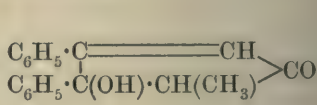
* Although this conclusion happened to be correct, we have since convinced ourselves that, except in the case of acid derivatives of anhydracetonebenzil, which may be dissolved in a solution of sodium carbonate before applying the permanganate test, the difference in the rate of oxidation is not sufficiently marked to serve as a means of distinguishing with certainty between the two classes. The open-chain condensation compounds of benzil with ketones may, however, be distinguished from anhydracetonebenzil derivatives by the much greater ease with which they are attacked by permanganate.

In the case of the monoalkyl anhydracetonebenzils, the α-compounds are more soluble, and melt lower, than the corresponding β-compounds.

In the condensation of benzil with methyl ethyl ketone, there is formed, in addition to α-methylanhydracetonebenzil (m. p. 118°) and β-methylanhydracetonebenzil (m. p. 180·5°), a third isomeride melting at 157°. Its formation was only once observed in the original condensation, but it can be prepared from the β-compound by leaving the latter for a month in contact with cold alcoholic 0·5 per cent. potassium hydroxide, or by boiling it with glacial acetic acid. In both cases, the transformation is only partial, and, moreover, the resulting compound is partially retransformed into β-methylanhydracetonebenzil by allowing it to stand with alcoholic potassium hydroxide in the cold, so that there is evidently an equilibrium. By heating alone at 330°, it is totally converted into β-methylanhydracetonebenzil. We regard this compound as *desylene-methyl ethyl ketone*—probably the fumaroid form,  . In its transformation into β-methylanhydracetonebenzil, it would first pass into the maleoid form, which would then undergo internal aldol condensation:



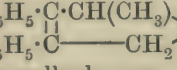
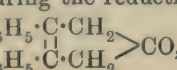
Maleoid form.



β-Methylanhydracetonebenzil (m. p. 180°).

That this compound is not a stereoisomeride of β-methylanhydracetonebenzil is, we consider, proved by the fact that it is so much more readily attacked by permanganate than the latter compound. The substance is, however, difficult to obtain in quantity, so that we have not been able to make a detailed study of its reactions, and we therefore put forward the above formula with reserve.

A similar open-chain isomeride of αβ-dimethylanhydracetonebenzil is described later on.

By boiling either α- or β-methylanhydracetonebenzil for a few minutes with fuming hydriodic acid, *methyldiphenyl*cyclo*pentenone*,  (m. p. 77—78°), was obtained. It yields a phenylhydrazone. The same migration of the double bonds occurs during the reduction as in the formation of diphenyl*cyclo*pentenone,  , from anhydracetonebenzil. The symmetrical con-

stitution of the latter *cyclo*pentenone was proved by Japp and Lander (Trans., 1897, **71**, 132) by oxidising it to diphenylmaleic acid.

By boiling α-methylanhydracetonebenzil for 5 hours with hydriodic acid and red phosphorus, it was completely reduced to 1-*methyl*-2 : 3-*diphenyl*cyclo*pentane*, $\begin{matrix} C_6H_5\cdot CH\cdot CH(CH_3) \\ C_6H_5\cdot CH\text{———}CH_2 \end{matrix}\!>\!CH_2$ (m. p. 62—63°), already obtained by Japp and Murray (Trans., 1897, **71**, 152), by the reduction of α-anhydracetonebenzillævulic acid, the carboxyl group of the acid being eliminated in the latter case.

α-Methylanhydracetonebenzil, like anhydracetonebenzil itself, readily interacts with benzaldehyde under the influence of alcoholic potassium hydroxide in the cold, yielding a benzylidene derivative. *Benzylidene-α-methylanhydracetonebenzil* (m. p. 225°) has the constitution

$$\begin{matrix} C_6H_5\cdot C\!:\!C(CH_3) \\ C_6H_5\cdot C(OH)\text{—}C \end{matrix}\!>\!CO$$
$$\qquad\qquad\quad =CH\cdot C_6H_5$$

The other α-alkylanhydracetonebenzils yield similar benzylidene derivatives.

When β-methylanhydracetonebenzil, on the other hand, is allowed to stand with benzaldehyde and alcoholic potassium hydroxide, there is, at first, apparently no action. After the mixture has stood for a month, however, it is found that a portion of the β-methylanhydracetonebenzil has been converted into the open-chain compound desylene-methyl ethyl ketone* (m. p. 157°) already referred to, whilst a very small quantity of the benzylidene derivative of α-methylanhydracetonebenzil has been formed. This means that, in presence of the potassium hydroxide, a portion of the β-methylanhydracetonebenzil is hydrolysed to benzil and methyl ethyl ketone (the formation of the open-chain compound being an intermediate stage), and that these products of hydrolysis again interact, yielding, in part at least, α-methylanhydracetonebenzil, which then undergoes condensation with the benzaldehyde.

α-Methylanhydracetonebenzil and benzil interact, in presence of alcoholic potassium hydroxide, to form *α-methylanhydracetonedibenzil*, $C_{32}H_{26}O_4$ (dimorphous ; silky needles, m. p. 185° ; and warty crystals, m. p. 194°),

$$C_{18}H_{16}O_2 + C_{14}H_{10}O_2 = C_{32}H_{26}O_4,$$

which is obtained in the form of the complex *potassium* salt, $C_{32}H_{25}O_4K, C_{32}H_{26}O_4, 4C_2H_5\cdot OH$. From this salt, the free substance is obtained by treating it with acetic acid. α-Methylanhydracetonedi-

* We at first took this substance for an aldol condensation compound of benzaldehyde with β-methylanhydracetonebenzil (see Trans., 1899, **76**, 1020, footnote). The difference in percentage composition is but small.

benzil may be more simply prepared by the action of an alcoholic solution of sodium ethoxide on a mixture of benzil (2 mols.) with methyl ethyl ketone (1 mol.):

$$2\begin{matrix}C_6H_5\cdot CO\\ C_6H_5\cdot CO\end{matrix} + CH_3\cdot CO\cdot C_2H_5 = C_{32}H_{26}O_4 + H_2O,$$

the substance being thus obtained in the form of its *sodium* salt. When α-methylanhydracetonedibenzil is boiled with alcohol containing a few drops of sulphuric acid, it is esterified, yielding the compound $C_{32}H_{25}(OC_2H_5)O_3$ (m. p. 250°). In yielding salts with caustic alkalis, and in being esterified under the foregoing conditions, α-methylanhydracetonedibenzil resembles ethyl anhydrodibenzilacetoacetate (Japp and Lander, Trans., 1896, **69**, 736), and differs entirely from the corresponding compound from acetone and benzil—anhydracetonedibenzil, $C_{31}H_{24}O_4$—of which it might otherwise appear to be the next higher homologue.

By boiling α-methylanhydracetonebenzil with sulphuric acid somewhat diluted with water, or with glacial acetic acid, a dehydration product, $C_{36}H_{28}O_2$ (m. p. 230°, with evolution of gas), is formed according to the equation

$$2C_{18}H_{16}O_2 - 2H_2O = C_{36}H_{28}O_2.$$

The molecular weight of the resulting compound is doubled in order to bring it into line with the corresponding compound, $C_{24}H_{24}O_2$, from anhydracetonebenzil (Japp and Lander, Trans., 1897, **71**, 131). β-Methylanhydracetonebenzil is converted into the same dehydration product, $C_{36}H_{28}O_2$, by heating it in a sealed tube with anhydrous formic acid; whereas glacial acetic acid, as already mentioned, transforms it into desylene-methyl ethyl ketone.

Experimental.

Condensation of Benzil with Methyl Ethyl Ketone.

Preparation of α-Methylanhydracetonebenzil, $\begin{matrix}C_6H_5\cdot C{=}C(CH_3)\\ C_6H_5\cdot C(OH)\cdot CH_2\end{matrix}\!\!>\!CO$, *and β-Methylanhydracetonebenzil,* $\begin{matrix}C_6H_5\cdot C{=\!=\!=}CH\\ C_6H_5\cdot C(OH)\cdot CH(CH_3)\end{matrix}\!\!>\!CO$.—These compounds are formed by the condensation of benzil with methyl ethyl ketone under the influence of potassium hydroxide. With alcoholic potassium hydroxide, the α-compound is almost the sole product; with aqueous potassium hydroxide, the β-compound slightly predominates.

In the preparation of the α-compound, 10 grams of finely powdered benzil, 7 grams of methyl ethyl ketone, and 100 c.c. of alcoholic 0·5

per cent. potassium hydroxide (4 grams KOH to 1 litre of absolute alcohol *) were introduced into a flask which was then corked and, after dissolving the benzil by shaking, allowed to stand. The experiment was so arranged that the liquid nearly filled the flask and that the quantity of alcohol was just sufficient to dissolve the benzil. After standing at the ordinary temperature for 17 days, the liquid, from which nothing had been deposited, was poured into a large bulk of water; this occasioned the separation of an oil, which speedily solidified to a mass of almost white crystals of the α-compound. After a single crystallisation from hot alcohol, the substance was pure. It formed large, flat, lozenge-shaped crystals melting at 118°. It is readily soluble both in alcohol and in ether.

Analysis of *α-methylanhydracetonebenzil* gave figures agreeing with the formula $C_{18}H_{16}O_2$:

0·1585 gave 0·4734 CO_2 and 0·0866 H_2O. C = 81·47; H = 6·07.
0·1402 ,, 0·4187 CO_2 ,, 0·0781 H_2O. C = 81·45; H = 6·19.
$C_{18}H_{16}O_2$ requires C = 81·82; H = 6·06 per cent.

The yield from the above quantities was 8 grams, and the alcoholic mother liquor gave a small amount—considerably less than a gram—of the isomeric β-methylanhydracetonebenzil already obtained by Japp and Burton.

In order to prepare β-methylanhydracetonebenzil in quantity, the method employed by Japp and Burton (*loc. cit.*) was, with slight modifications, adopted. Forty grams of benzil, 25 grams of methyl ethyl ketone, and 30 c.c. of *aqueous* potassium hydroxide of 33·3 per cent. strength were introduced into a conical flask fitted with a condensing tube, the whole being placed on a metal plate over a water-bath and heated for 9 hours, shaking from time to time. The mixture, which had become brown, was poured into excess of hot water. The solidified substance was ground, washed with water, and well extracted with cold ether. The residue was dissolved in boiling alcohol; on cooling, prismatic crystals of *β-methylanhydracetonebenzil* were deposited, which, after two or three recrystallisations, melted constantly at 180° (179°, Japp and Burton). The alcoholic mother liquor gave a small quantity of octahedral crystals melting at 157°, of a substance which is isomeric with the two foregoing, and which we regard as desylenemethyl ethyl ketone (*v. infra*). The ethereal extract gave a considerable quantity of α-methylanhydracetonebenzil (m. p. 118°).

In the foregoing experiment, the quantity of α-compound obtained

* Absolute alcohol should be used in these condensations. "Methylated spirit" (alcohol "denatured" with crude wood spirit; compare Trans., 1897, **71**, 297, footnote) must be avoided, as it contains acetone, which yields condensation compounds of its own with benzil.

was 8·5 grams, and of β-compound, 11 grams. Longer heating diminished the proportion of the β-compound, and in addition, the resinous bye-products rendered the substances more difficult to purify.

β-Methylanhydracetonebenzil has already been analysed by Japp and Burton.

Molecular Weights of α- and β-Methylanhydracetonebenzil.—The molecular weights of the two compounds were determined by Walker and Lumsden's modification of Landsberger's ebullioscopic method, using alcohol (constant = 1560) as a solvent.

α-Methylanhydracetonebenzil.

Substance.	Elevation.	Volume.	Mol. wt.
0·908	0·32°	16·6 c.c.	267.
,,	0·24	22·4 ,,	263.

$C_{18}H_{16}O_2 = 264.$

β-Methylanhydracetonebenzil.

0·896	0·292°	15·6 c.c.	308.
,,	0·210	22·2 ,,	300.

$C_{18}H_{16}O_2 = 264.$

The two substances are therefore isomeric.

Benzylidene-α-methylanhydracetonebenzil, $\begin{matrix} C_6H_5\cdot C{:}C(CH_3)>CO \\ C_6H_5\cdot C(OH)-C=CH\cdot C_6H_5 \end{matrix}$.—Five grams of α-methylanhydracetonebenzil, 2·5 grams of benzaldehyde, and 65 c.c. of alcoholic potassium hydroxide (0·5 per cent.) were mixed, shaken until all had dissolved, and allowed to stand. Overnight, tufts of needle-shaped crystals had formed; after 4 days they were separated and recrystallised from hot glacial acetic acid, from which the substance was deposited in colourless, slender, rectangular prisms melting at 225°. (Yield 3·6 grams.)

0·1608 gave 0·5018 CO_2 and 0·0839 H_2O. C = 85·11; H = 5·80.

$C_{25}H_{20}O_2$ requires C = 85·23; H = 5·68 per cent.

β-Methylanhydracetonebenzil, when subjected to the above treatment for the same time, is quite unchanged. Its behaviour on long standing with the mixture is mentioned in the introduction.

Conversion of β-Methylanhydracetonebenzil into Desylene-methyl Ethyl Ketone, $\begin{matrix} C_6H_5\cdot C{:}CH\cdot CO\cdot C_2H_5 \\ C_6H_5\cdot CO \end{matrix}$.—The best mode of effecting this transformation is by boiling β-methylanhydracetonebenzil with four times its weight of glacial acetic acid for 4 hours. The solution, on cooling, deposits needles or prisms of unchanged substance; and from the

mother liquor, octahedral crystals of the open-chain compound, melting at 157°, may be obtained.

The same compound is also slowly formed when finely powdered β-methylanhydracetonebenzil is allowed to stand for a month or more with alcoholic potassium hydroxide (0·5 KOH per cent.) insufficient to dissolve it. The transformation is incomplete, as the reaction is reversible (see introduction).

The formation of the same compound was also observed in the preparation of β-methylanhydracetonebenzil (*v. supra*).

Analysis of the octahedral crystals (m. p. 157°) showed that the substance, which we regard as *desylene-methyl ethyl ketone*, is isomeric with α- and β-methylanhydracetonebenzil.

0·1485 gave 0·4431 CO_2 and 0·0798 H_2O. C = 81·36 ; H = 5·97.
0·1629 „ 0·4862 CO_2 „ 0·0903 H_2O. C = 81·39 ; H = 6·16.
$C_{18}H_{16}O_2$ requires C = 81·82 ; H = 6·06 per cent.

The reason for regarding this compound as structurally different from the methylanhydracetonebenzils is that it is much more readily attacked by permanganate.

A small quantity of the compound was heated in an exhausted tube for a short time at 330°. There was no sign of decomposition, and the melted substance began to distil and collect in the cooler part of the tube. On crystallising the product from alcohol, it was found that it had been re-converted into β-methylanhydracetonebenzil (m. p. 180°).

α-Methylanhydracetonebenzil is quite unchanged by contact with alcoholic potassium hydroxide of the above strength. Boiling with glacial acetic acid dehydrates it, yielding the compound, $C_{36}O_{28}O_2$, melting at 230° (*v. infra*).

Action of Dehydrating Agents on α- and β-Methylanhydracetonebenzil.—One gram of α-methylanhydracetonebenzil was boiled for half-an-hour with 5 c.c. of sulphuric acid diluted with 10 c.c. of water, employing a reflux condenser. From the product, which was very dark coloured, crystals melting at 230° were obtained. The following method yields the substance in a purer state.

One gram of α-methylanhydracetonebenzil was boiled with 4 grams of glacial acetic acid for 4 hours. On cooling, the liquid deposited a crystalline compound which proved to be identical with that obtained by the action of hot dilute sulphuric acid. Recrystallised, first from glacial acetic acid and afterwards from amyl alcohol, it formed minute, very lustrous, oblique prisms or plates, melting, when rapidly heated, at 230°, with evolution of gas—doubtless carbon monoxide, to judge from the analogy of the corresponding compound, $C_{34}H_{24}O_2$, obtained from anhydracetonebenzil (Japp and Burton, Trans., 1887, 51, 426). It is sparingly soluble in solvents of low boiling point.

Analysis gave figures agreeing with those required for the formula $C_{36}H_{28}O_2$.

0·1321 gave 0·4240 CO_2 and 0·0734 H_2O. C = 87·54; H = 6·18.

$C_{36}H_{28}O_2$ requires C = 87·82; H = 5·69 per cent.

β-Methylanhydracetonebenzil is not altered by boiling with sulphuric acid of the foregoing strength, whilst a stronger acid chars it. Boiling it with acetic acid, and even heating with the acid in a sealed tube at 130°, gave only desylene-methyl ethyl ketone. Heating with formic acid, however, converts it into the compound $C_{36}H_{28}O_2$.

Four grams of β-methylanhydracetonebenzil and 16 grams of concentrated formic acid were heated in a sealed tube at 130° for 4 hours. The products were a pasty solid and a violet coloured liquid. The solid was dissolved in benzene, and light petroleum was added, which precipitated resinous matter. The filtrate yielded lustrous crystals of the compound $C_{36}H_{28}O_2$, which, after recrystallisation from acetic acid, melted at 230° with evolution of gas.

α- and β-Methylanhydracetonebenzil thus yield the same compound, $C_{36}H_{28}O_2$, by elimination of the elements of water. The reason for doubling the formula of this substance is given in the introduction.

Reduction of α- and β-Methylanhydracetonebenzil with Hydriodic Acid: Formation of Methyldiphenylcyclopentenone, $\begin{matrix} C_6H_5\cdot C\cdot CH(CH_3) \\ C_6H_5\cdot C\text{———}CH_2 \end{matrix}\!>\!CO$, *and* 1-*Methyl*-2 : 3-*diphenylcyclopentane,* $\begin{matrix} C_6H_5\cdot CH\cdot CH(CH_3) \\ C_6H_5\cdot CH\text{———}CH_2 \end{matrix}\!>\!CH_2$.—Ten grams of α-methylanhydracetonebenzil were boiled with excess of fuming hydriodic acid (sp. gr. 1·9) for 5 minutes. Excess of water was added, and the solid substance, separated by filtration, was dissolved in ether. The ethereal solution was shaken with dilute sulphurous acid, then with a solution of sodium carbonate, and dried with calcium chloride. On spontaneous evaporation, it gave crystals which, after repeated recrystallisation from light petroleum, were obtained in the form of faint yellow, oblique, flat prisms or plates melting constantly at 77—78°.

In another experiment, the residue which remained after expelling the ether was distilled under reduced pressure. The crude product passed over at about 200° under a pressure of 12 mm. This procedure considerably facilitated the purification of the substance, but was attended with loss. The compound was finally crystallised from light petroleum. It melted, as above, at 77—78°.

Analysis gave figures agreeing with those required for a *methyldiphenylcyclopentenone*, $C_{18}H_{16}O$.

0·1936 gave 0·6179 CO_2 and 0·1146 H_2O. C = 87·04; H = 6·58.

0·1730 „ 0·5524 CO_2 „ 0·1013 H_2O. C = 87·08; H = 6·50.

$C_{18}H_{16}O$ requires C = 87·10; H = 6·45 per cent.

β-Methylanhydracetonebenzil was then reduced in precisely the same way with hydriodic acid. It yielded the same methyldiphenyl-*cyclo*pentenone melting at 77—78°. A supersaturated solution of the compound thus prepared instantly crystallised on adding a little of the crystalline compound obtained from α-methylanhydracetonebenzil.

Methyldiphenyl*cyclo*pentenone forms a *phenylhydrazone*,

$$\begin{matrix} C_6H_5\cdot C\cdot CH(CH_3) \\ C_6H_5\cdot C\!\!-\!\!-\!\!CH_2 \end{matrix}\!\!>\!C\!:\!N\cdot NH\cdot C_6H_5.$$

In preparing this compound, 1 gram of methyldiphenyl*cyclo*pentenone was heated with 1 gram of phenylhydrazine and about 6 c.c. of alcohol in a sealed tube for 5 hours at 100°. Addition of dilute acetic acid and, subsequently, of water, caused the separation of an oil; this was dissolved in warm alcohol. The solution deposited clusters of minute, yellow prisms melting with decomposition at from 145° to 152° according to the rate of heating. It decomposes on recrystallisation.

Analysis gave figures agreeing with those required for the foregoing *phenylhydrazone*.

0·1181 gave 8·5 c.c. moist nitrogen at 13·5° and 757 mm. N = 8·46.
$C_{24}H_{22}N_2$ requires N = 8·28 per cent.

In order to carry the reduction further than the formation of methyldiphenyl*cyclo*pentenone, and to obtain, if possible, the corresponding *cyclo*pentane derivative, 10 grams of α-methylanhydracetonebenzil were boiled with 150 grams of hydriodic acid (sp. gr. 1·7) and 20 grams of red phosphorus for 5 hours. The product was worked up as described in the foregoing reduction experiments, removing iodine and then distilling under reduced pressure. A large fraction passed over between 160° and 200° under 20 mm. pressure; on standing, it solidified. On dissolving it in ether and adding methyl alcohol, tufts of colourless, slender needles separated; after recrystallising twice from the same solvents, they melted constantly at 62—63°. The substance was identical with the 1-*methyl*-2:3-*diphenyl*cyclo*pentane* obtained by Japp and Murray (Trans., 1897, 71, 153) by the reduction of α-anhydrobenzillævulic acid. A specimen prepared in the latter way at once started the crystallisation of a supersaturated solution of the present compound.

0·1791 gave 0·5990 CO_2 and 0·1380 H_2O. C = 91·20; H = 8·56.
$C_{18}H_{20}$ requires C = 91·52; H = 8·48 per cent.

Condensation of α-Methylanhydracetonebenzil with Benzil; Formation of α-Methylanhydracetonedibenzil, $C_{32}H_{26}O_4$.—The fact that anhydracetonebenzil interacts with benzil in presence of dilute alcoholic potassium hydroxide to form an aldol condensation compound, anhydr-

acetonedibenzil (Japp and Findlay, Trans., 1899, 75, 1025), led us to try whether α-methylanhydracetonebenzil would exhibit an analogous behaviour.

In our first experiment, we used the very dilute alcoholic potassium hydroxide which had proved efficacious in the previous condensations. The reaction took place ; but as the product proved to be a potassium salt, and as there was not sufficient potassium hydroxide present to form this salt with the whole of the other interacting substances, we repeated the experiment, using a stronger solution of the hydroxide, and obtained a much better result.

3·3 grams of α-methylanhydracetonebenzil and 2·5 grams of benzil were dissolved in 32 c.c. of alcoholic potassium hydroxide (2 grams of KOH to 100 c.c. of absolute alcohol). The solution was filtered into a small flask, which was corked up and the whole allowed to stand. (As the potassium salt cannot be recrystallised without decomposing it, it is necessary to obtain it pure at once.) After 4 days, there was a deposit of large, well-developed crystals ; these were separated, washed with cold alcohol, and air-dried by brief exposure on filter-paper. They effloresce on standing. The compound is a *potassium* salt of *α-methylanhydracetonedibenzil*, $C_{32}H_{26}O_4$, and has the complex formula $C_{32}H_{25}O_4K,C_{32}H_{26}O_4,4C_2H_5\cdot OH$. Like the sodium salt of ethyl anhydrodibenzilacetoacetate (Japp and Lander, Trans., 1896, 69, 736), it is readily soluble in benzene and is totally decomposed by boiling with alcohol.

The potassium was determined in the ordinary way as sulphate ; the α-methylanhydracetonedibenzil by shaking a benzene solution of the salt with dilute hydrochloric acid, washing with water, and afterwards freeing from moisture and benzene, a process which could give only an approximate result ; and the alcohol of crystallisation by leaving the substance in a vacuum desiccator over sulphuric acid for 6 weeks, heating being inadmissible. The potassium determinations were made with different preparations.

0·5784 gave 0·0414 K_2SO_4. K = 3·21.
0·7854 „ 0·0566 K_2SO_4. K = 3·23.
2·0933 „ 1·737 $C_{32}H_{26}O_4$. $C_{32}H_{26}O_4$ = 82·97.
1·3482 lost, on drying, 0·2070. $C_2H_5\cdot OH$ = 15·35.
$C_{32}H_{25}O_4K,C_{32}H_{26}O_4,4C_2H_6O$ requires K = 3·33 ; $C_{32}H_{26}O_4$ = 81·02 ; C_2H_6O = 15·72 per cent.

The *sodium* salt, which was not analysed, was obtained direct from benzil and methyl ethyl ketone. Ten grams of benzil and 6·8 grams of methyl ethyl ketone were added to 200 c.c. of absolute alcohol in which 4·4 grams of sodium had previously been dissolved. There was a slight rise of temperature and the benzil went into solution. After

standing overnight in a corked flask, the liquid had deposited a large quantity of needle-shaped crystals. The substance was worked up for α-methylanhydracetonedibenzil after standing for 3 days. It was identical with a sodium salt which we obtained by condensing α-methylanhydracetonebenzil with benzil by means of an alcoholic solution of sodium ethoxide.

In order to obtain free α-methylanhydracetonedibenzil, either the potassium or the sodium salt, prepared as already described, is washed with cold alcohol and dissolved in benzene in the cold. By adding glacial acetic acid until the solution has an acid reaction and then shaking with water, the alkali metal is removed. The α-methylanhydracetonedibenzil soon begins to separate in a crystalline form from the benzene solution; it is purified by recrystallisation from boiling alcohol. Two kinds of crystals are obtained: from the hot alcoholic solution, small, hard warty crystals melting at 194°; from the cold solution, silky needles melting at 185°. The two forms may be readily changed one into the other, and neither contains solvent of crystallisation. The same two forms are deposited from a benzene solution.

On analysis, the substance gave figures agreeing with those required for the formula of *α-methylanhydracetonedibenzil*, $C_{32}H_{26}O_4$. Analysis I was made with the needles; analysis II with the warty crystals.

0·1488 gave 0·4396 CO_2 and 0·0748 H_2O. C = 80·57; H = 5·58.
0·1472 „ 0·4352 CO_2 „ 0·0750 H_2O. C = 80·63; H = 5·66.
$C_{32}H_{26}O_4$ requires C = 81·01; H = 5·48 per cent.

Like its analogue, ethyl anhydrodibenzilacetoacetate, it is difficult to burn.

As the composition of the potassium salt of α-methylanhydracetonedibenzil might be taken as pointing to a molecular weight twice as great as that represented by the formula $C_{32}H_{26}O_4$, an ebullioscopic determination of the molecular weight was made by the method already referred to, using alcohol (constant = 1560) as a solvent.

α-Methylanhydracetonedibenzil.

Substance.	Elevation.	Volume.	Mol. wt.
0·613	0·13°	17·5 c.c.	420
„	0·10	22·5	425

$C_{32}H_{26}O_4 = 474$.

This result decides in favour of the lower molecular weight.

Ethylation of α-Methylanhydracetonedibenzil.—The fact that a hydrogen atom in ethyl anhydrodibenzilacetoacetate may be replaced by ethyl by boiling the compound with alcohol containing a few drops of

sulphuric acid (Japp and Lander, Trans., 1896, 69, 738) led us to try the same experiment with α-methylanhydracetonedibenzil.

Five grams of α-methylanhydracetonedibenzil, 100 c.c. of absolute alcohol, and 5 drops of concentrated sulphuric acid were boiled, using a reflux condenser. At first everything dissolved; but in a short time a separation of small crystals commenced, the amount of which gradually increased. After 3 hours, the operation was interupted; the crystals were separated and washed with alcohol. They formed very sparingly soluble, colourless, short needles, melting at 250°.

Analysis showed that an ethyl derivative, $C_{32}H_{25}(OC_2H_5)O_3$, had been formed.

0·1643 gave 0·4883 CO_2 and 0·0895 H_2O. C = 81·09; H = 6·05.
$C_{34}H_{30}O_4$ requires C = 81·27; H = 5·98 per cent.

Condensation of Benzil with other Ketones.

The condensations remaining to be described were all carried out by the methods already given for the preparation of α- and β-methylanhydracetonebenzil, the condensing agent being either alcoholic 0·5 per cent. potassium hydroxide (4 grams KOH to 1 litre of absolute alcohol) in the cold, or aqueous 33·3 per cent. potassium hydroxide at a temperature somewhat under 100° (see preparation of β-methylanhydracetonebenzil). Where two isomeric condensation compounds are formed, the former method generally gives, as already mentioned, the better yield of the compound of lower melting point. The separation of the two isomerides was effected by fractional crystallisation from alcohol, occasionally preceded by extraction of the more soluble isomeride with ether.

α-Desylene-ethyl Ethyl Ketone, $\begin{matrix} C_6H_5\cdot C\cdot C(CH_3)\cdot CO\cdot C_2H_5 \\ \quad\quad\quad\

aqueous potassium hydroxide (33·3 per cent.), 30 c.c. Time of heating 24 hours. (For mode of heating and of working up, see preparation of β-methylanhydracetonebenzil.) The products were the same as in the previous experiment, but the proportion of αβ-dimethylanhydracetonebenzil was greater. The yield of this compound was 27 grams.

αβ-Dimethylanhydracetonebenzil crystallises from alcohol in colourless, rhomboidal plates or prisms, melting at 150°, as described by Japp and Burton (*loc. cit.*), by whom it was prepared and analysed.

α-Desylene-ethyl ethyl ketone is deposited from alcohol in large, oblique, four-sided prisms melting at 128°. Analysis showed that it was isomeric with the preceding compound.

0·1649 gave 0·4943 CO_2 and 0·0967 H_2O. C = 81·75 ; H = 6·52.
0·1670 „ 0·5012 CO_2 „ 0·0988 H_2O. C = 81·85 ; H = 6·57.
$C_{19}H_{18}O_2$ requires C = 82·01 ; H = 6·48 per cent.

α-Desylene-ethyl ethyl ketone is much more readily attacked by permanganate than αβ-dimethylanhydracetonebenzil, indicating that it is structurally different from, not merely stereoisomeric with, the latter compound. It is probably fumaroid α-desylene-ethyl ethyl ketone, as the maleoid form might be expected to undergo internal aldol condensation to αβ-dimethylanhydracetonebenzil under the influence of potassium hydroxide. This change, however, takes place under the influence of heat. A small quantity of α-desylene-ethyl ethyl ketone was heated in an atmosphere of carbon dioxide at 300—320° for 10 minutes. The fused mass, which had turned light brown, was dissolved in alcohol; on seeding the solution with a trace of αβ-dimethylanhydracetonebenzil, it began to crystallise and deposited the characteristic rhomboidal plates of that substance, melting at 149° (m. p. 150°). The transformation occurs as follows:

$$\begin{matrix} C_6H_5\cdot C\!:\!C(CH_3)\cdot CO\cdot CH_2\cdot CH_3 \\ C_6H_5\cdot CO \end{matrix} = \begin{matrix} C_6H_5\cdot C\!=\!\!=\!\!=\!C(CH_3) \\ C_6H_5\cdot C(OH)\cdot CH(CH_3) \end{matrix} > CO$$

α-Desylene-ethyl ethyl ketone (m. p. 128°). — αβ-Dimethylanhydracetonebenzil (m. p. 150°).

The former compound thus corresponds with desylene-methyl ethyl ketone, which under the influence of heat is converted into β-methylanhydracetonebenzil (*v. supra*).

It may be noted that the transformation of α-desylene-ethyl ethyl ketone into αβ-dimethylanhydracetonebenzil does not take place when the substance is heated in a vacuum, as under these circumstances it distils without change.

ββ-Dimethylanhydracetonebenzil, $\begin{matrix} C_6H_5\cdot C\!=\!\!=\!\!=\!CH \\ C_6H_5\cdot C(OH)\cdot C(CH_3)_2 \end{matrix} > CO$.—Only the method with alcoholic potassium hydroxide was employed. The

proportions were: benzil, 10 grams; methyl *iso*propyl ketone, 7·5 grams; alcoholic potassium hydroxide (0·5 per cent.), 125 c.c. The reaction was allowed to go on at the ordinary temperature. Crystals of the new compound separated within a day. After standing for three days, the product was worked up in the usual way. It crystallised from alcohol in clusters of prisms, with pyramidal ends, or in plates, melting at 181°. Only this one substance was formed in the reaction.

Analysis gave figures agreeing with the formula of *ββ-dimethylanhydracetonebenzil.*

0·1789 gave 0·5358 CO_2 and 0·1059 H_2O. C = 81·68; H = 6·58.
0·1326 „ 0·3968 CO_2 „ 0·0810 H_2O. C = 81·62; H = 6·80.
$C_{19}H_{18}O_2$ requires C = 82·01; H = 6·48 per cent.

That the compound is not an open-chain diketone follows from its high melting point.* That it is ββ-dimethylanhydracetonebenzil is shown by the product which it yields on oxidation. This will be described in a subsequent paper.

α-Ethylanhydracetonebenzil, $\begin{matrix} C_6H_5\cdot C = C(C_2H_5) \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{matrix}\!\!>\!CO$, *and β-Ethylanhydracetonebenzil,* $\begin{matrix} C_6H_5\cdot C \equiv\equiv CH \\ C_6H_5\cdot C(OH)\cdot CH(C_2H_5) \end{matrix}\!\!>\!CO$. — Forty grams of benzil, 30 grams of methyl *n*-propyl ketone, and 30 c.c. of aqueous 33·3 per cent. potassium hydroxide were heated for 16 hours in the way already described. The product, precipitated with water, washed with ether, and recrystallised from alcohol, formed minute needles melting at 156°, and was identical with the *β-ethylanhydracetonebenzil* prepared and analysed by Japp and Burton (*loc. cit.*). The ethereal extract gave a more soluble substance which crystallised from alcohol in large prisms, sometimes obliquely truncated, sometimes with pyramidal ends, melting at 114°. This proved to be *α-ethylanhydracetonebenzil.*

In a second experiment, 10 grams of benzil, 7·5 grams of methyl *n*-propyl ketone, and 125 c.c. of alcoholic potassium hydroxide (0·5 per cent.) were mixed and allowed to stand at the ordinary temperature for a month, although a shorter time would doubtless have sufficed. The solution had turned brown. The same products were obtained as in the previous experiment, but the yield of the α-compound was better.

Analysis of α-ethylanhydracetonebenzil (m. p. 114°) gave figures agreeing with those required for the formula $C_{19}H_{18}O_2$.

* Thus α-benzoyl-β-trimethacetylstyrene, $\begin{matrix} C_6H_5\cdot C{:}CH\cdot CO\cdot C(CH_3)_3 \\ C_6H_5\cdot CO \end{matrix}$, from benzil and methyl *tert.* butyl ketone (to be described in a later communication), melts as low as 115°.

0·1756 gave 0·5276 CO_2 and 0·1036 H_2O. C = 81·93 ; H = 6·55.
0·1644 „ 0·4934 CO_2 „ 0·0974 H_2O. C = 81·85 ; H = 6·58.
$C_{19}H_{18}O_2$ requires C = 82·01 ; H = 6·48 per cent.

Benzylidene-α-ethylanhydracetonebenzil, $\begin{matrix} C_6H_5\cdot C\cdot C(C_2H_5) \\ C_6H_5\cdot C(OH)-C \end{matrix}\!\!>\!CO$.
$\quad\quad\quad

αββ-trimethylanhydracetonebenzil, since all the open-chain compounds formed in these condensations are converted on heating into the isomeric closed chain derivatives. The question could be finally settled only by a study of the reactions of the compound, but the difficulty of obtaining the necessary ethyl *iso*propyl ketone, and the smallness of the yield of the condensation product, make this for the present impossible.

α-n-*Propylanhydracetonebenzil*, $\begin{matrix}C_6H_5\cdot C=C(C_3H_7)\\ C_6H_5\cdot C(OH)\cdot CH_2\end{matrix}>CO$, and *β*-n-*Propylanhydracetonebenzil*, $\begin{matrix}C_6H_5\cdot C\equiv CH\\ C_6H_5\cdot C(OH)\cdot CH(C_3H_7)\end{matrix}>CO$.—In the first experiment, 40 grams of benzil, 34 grams of methyl *n*-butyl ketone, and 30 c.c. of 33·3 per cent. aqueous potassium hydroxide were heated for 34 hours. The process was carried out as in the preparation of *β*-methylanhydracetonebenzil. In working up the product, the ethereal extract gave a substance which was deposited from ether in large, flat, obliquely truncated prisms, and from alcohol in six-sided plates, melting at 89°. This proved to be *α*-n-*propylanhydracetonebenzil*. The sparingly soluble residue, recrystallised from alcohol, was deposited in clusters of slender prisms melting at 152°. This was *β*-n-*propylanhydracetonebenzil*. It formed the chief product. The yield of purified *β*-compound was 12·5 grams.

In a second experiment, a mixture of 10 grams of benzil, 8·5 grams of methyl *n*-butyl ketone, and 125 c.c. of alcoholic potassium hydroxide (0·5 per cent.) was allowed to stand in a corked flask at the ordinary temperature for a month. The products were the same as in the former case, but the yield of *α-n*-propylanhydracetonebenzil was better.

Analysis of *α-n*-propylanhydracetonebenzil (m. p. 89°):

0·1783 gave 0·5372 CO_2 and 0·1077 H_2O. C = 82·19; H = 6·73.
0·1813 „ 0·5440 CO_2 „ 0·1162 H_2O. C = 81·83; H = 7·12.
$C_{20}H_{20}O_2$ requires C = 82·19; H = 6·85 per cent.

Analysis of *β-n*-propylanhydracetonebenzil (m. p. 152°):

0·1836 gave 0·5530 CO_2 and 0·1121 H_2O. C = 82·13; H = 6·78.
0·1850 „ 0·5570 CO_2 „ 0·1151 H_2O. C = 82·12; H = 6·90.
$C_{20}H_{20}O_2$ requires C = 82·19; H = 6·85 per cent.

Benzylidene-α-n-*propylanhydracetonebenzil*, $\begin{matrix}C_6H_5\cdot C:C(C_3H_7)\\ C_6H_5\cdot C(OH)-C=CH\cdot C_6H_5\end{matrix}>CO$—The condensation of *α-n*-propylanhydracetonebenzil with benzaldehyde was carried out as in the case of the other *α*-compounds, the reaction taking place in this case also in the cold. The benzylidene derivative was deposited from its hot alcoholic solution in clusters of small laminæ melting at 166°.

0·1591 gave 0·4970 CO_2 and 0·0930 H_2O. C = 85·19 ; H = 6·49.
$C_{27}H_{24}O_2$ requires C = 85·26 ; H = 6·32 per cent.

β-n-Propylanhydracetonebenzil did not interact with benzaldehyde.

αβ-Diethylanhydracetonebenzil, $\begin{matrix} C_6H_5\cdot C \!=\!\!=\!\!= C(C_2H_5) \\ C_6H_5\cdot C(OH)\cdot CH(C_2H_5) \end{matrix}\!\!>\!CO$.—When benzil and dipropyl ketone were heated with aqueous potassium hydroxide, no condensation took place. The action of alcoholic potassium hydroxide in the cold, however, gave the desired result.

A mixture of 10 grams of benzil, 10 grams of dipropyl ketone, and 125 c.c. of alcoholic potassium hydroxide (0·5 per cent.) was allowed to stand in a corked flask at the ordinary temperature for a month. On pouring the product into water, an oil separated which speedily became crystalline. By recrystallisation from alcohol, only one product could be obtained : plates of rhombic outline, striated parallel to the shorter diagonal, melting at 113—114°. It was not changed by heating for 10 minutes at 300—320° in an atmosphere of carbon dioxide, thus showing that it is not an open-chain compound.

Analysis gave figures agreeing with those required for the formula of *diethylanhydracetonebenzil*.

0·1453 gave 0·4379 CO_2 and 0·0943 H_2O. C = 82·19 ; H = 7·21.
0·2047 „ 0·6180 CO_2 „ 0·1328 H_2O. C = 82·33 ; H = 7·20.
$C_{21}H_{22}O_2$ requires C = 82·35 ; H = 7·19 per cent.

α-n-*Amylanhydracetonebenzil*, $\begin{matrix} C_6H_5\cdot C \!=\! C(C_5H_{11}) \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{matrix}\!\!>\!CO$, *and* *β*-n-*amylanhydracetonebenzil*, $\begin{matrix} C_6H_5\cdot C \!=\!\!=\!\!= CH \\ C_6H_5\cdot C(OH)\cdot CH(C_5H_{11}) \end{matrix}\!\!>\!CO$.—Forty grams of benzil, 44 grams of methyl *n*-hexyl ketone, and 30 c.c. of 33·3 per cent. aqueous potassium hydroxide were heated for 15 hours as described under the preparation of *β*-methylanhydracetonebenzil, the product being afterwards worked up in the usual way. Only *β-amylanhydracetonebenzil*—slender, silky needles melting at 150·5°, described and analysed by Japp and Burton—was obtained.

In a second experiment, a mixture of 10 grams of benzil, 11 grams of methyl *n*-hexyl ketone, and 125 c.c. of alcoholic potassium hydroxide (0·5 per cent.) was allowed to stand in a corked flask for a month. On pouring into water, the product which separated was partly crystalline, partly oily. The solid portion, after crystallisation from alcohol, yielded needles of *β*-amylanhydracetonebenzil melting at 150·5°. The oil, on long standing, also gave crystals—large, six-sided plates—which after recrystallising twice from light petroleum melted constantly at 57°, and proved to be the isomeric *α-amylanhydracetonebenzil*. The yield of the latter compound is fairly good.

Analysis of α-amylanhydracetonebenzil (m. p. 57°):

0·1763 gave 0·5338 CO_2 and 0·1210 H_2O. C = 82·56; H = 7·63.
0·1678 „ 0·5067 CO_2 „ 0·1142 H_2O. C = 82·35; H = 7·56.
$C_{22}H_{24}O_2$ requires C = 82·50; H = 7·50 per cent.

Benzylidene-α-amylanhydracetonebenzil, $\begin{matrix} C_6H_5\cdot C{:}C(C_5H_{11}){>}CO \\ C_6H_5\cdot C(OH){-}C{=}CH\cdot C_6H_5 \end{matrix}$—This compound was prepared like the other benzylidene derivatives of α-compounds. It is deposited from its solution in boiling alcohol in colourless needles melting at 156°.

0·1595 gave 0·4985 CO_2 and 0·1011 H_2O. C = 85·21; H = 7·04.
$C_{29}H_{28}O_2$ requires C = 85·29; H = 6·86 per cent.

β-Amylanhydracetonebenzil does not interact with benzaldehyde.

One of us is at present engaged, conjointly with Mr. Arthur C. Michie, in studying the products of the oxidation of the various methyl homologues of anhydracetonebenzil.

The foregoing two papers form a continuation of a general investigation of the reactions of ketonic compounds (compare Trans., 1897, 71, 123), and the expenses incidental to the work have for some years past been in part defrayed by various allotments from the Government Grant Fund of the Royal Society.

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CIX.—*The Direct Union of Carbon and Hydrogen. Part II.*

By WILLIAM A. BONE and DAVID S. JERDAN.

IN a previous paper on the subject (Trans., 71, 1897, 41) we showed that carbon and hydrogen combine at 1200° forming a saturated hydrocarbon; and further, that when the electric arc is passed between carbon terminals in an atmosphere of hydrogen, a saturated hydrocarbon is produced in addition to acetylene, the formation of each continuing until a definite equilibrium between the hydrocarbons, hydrogen, and carbon vapour is established. It was also shown that the same condition of equilibrium is attained when the arc is passed for some time in an atmosphere of either acetylene or methane under similar conditions.

We had not, however, separated the saturated hydrocarbon, or

hydrocarbons, formed at 1200°, or in the arc, from the large excess of hydrogen always present in the gases obtained in the various experiments, consequently we were unable to produce any experimental evidence as to either the number or character of the saturated hydrocarbons formed in either case. In absence of any such evidence, we provisionally assumed that the gases under examination contained no saturated hydrocarbon other than methane, and interpreted our analytical results accordingly.

We felt at the time that, so long as this question remained unsettled, the investigation of the subject could not be considered complete; circumstances, however, for a long time prevented our continuing the research, but during the past three years we have been continuously working on this and other points arising out of the earlier experiments. The present communication contains an account of a series of experiments which complete that part of our inquiry which refers to the character of the saturated hydrocarbons produced by the direct combination of their elements at 1200°, and in the arc, and the successful solution of this problem has proved a very tedious and difficult matter.

In order to avoid undue repetition of experimental details, we must refer the reader to the account given in our previous paper of the methods employed for the purification of the carbon and hydrogen required for the research, and also to the diagrams and explanations contained therein of the apparatus used both for the tube experiments at 1200° and for the arc experiments. Practically the same arrangements, with certain minor improvements which further experience suggested, were adopted for the experiments recorded in this paper.

The gas obtained by the interaction of carbon and hydrogen at 1200°, or in the arc, contained, in addition to small amounts of hydrocarbon, a relatively very large volume of hydrogen, as well as a small percentage of nitrogen. The latter was unavoidably introduced with the original hydrogen employed, and to some extent also during the course of the experiment. Obviously, therefore, the only feasible method of identifying the saturated hydrocarbon, or hydrocarbons, in such a mixture, was to remove first of all any unsaturated hydrocarbon present (for example, acetylene in the case of the arc gases), and afterwards the free hydrogen by means of palladium. There would then remain a mixture of the saturated hydrocarbon, or hydrocarbons, and nitrogen; an analysis of this mixture by explosion with excess of oxygen would reveal whether it contained one hydrocarbon only, or a mixture of hydrocarbons. If the evidence so obtained pointed to the former alternative, as it was found to do in the case of the gas from the experiments at 1200°, the analytical results would also indicate the nature of the hydrocarbon. If, on the other hand,

as in the case of the arc gases, the latter alternative were indicated, further investigation would be necessary.

After submitting the gases under investigation to the series of operations indicated in the preceding paragraph, we were able to show that methane is the only hydrocarbon formed from its elements at 1200°, and that the saturated hydrocarbons produced in the arc consist of a mixture of methane with another (or possibly others) of its homologues. The methods employed for the identification of this other saturated hydrocarbon will be fully explained later, at present it will be sufficient if we state that it ultimately proved to be ethane.

A. Examination of the Gas obtained by the action of Hydrogen on Solid Carbon in the Tube Experiments at 1200°.

Analyses published in the previous paper (pp. 49—51) had shown that the gases from the tube experiments contained no unsaturated hydrocarbon. It was therefore only necessary in this case to remove the diluting hydrogen in order to obtain the saturated hydrocarbon mixed with nitrogen only, This was accomplished by means of palladium black.

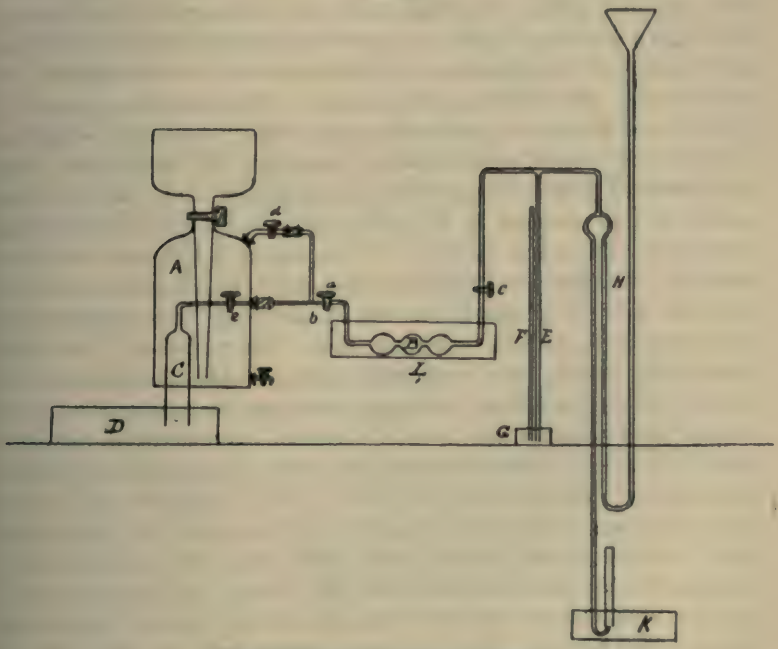
Three different experiments were performed in which hydrogen, free from hydrocarbons, was passed over pure carbon heated to 1200° in the jacketed porcelain tube described in the previous paper (pp. 46—51); a current of pure hydrogen was maintained through the jacket throughout each experiment. About 3 litres of the issuing gas were collected in each case in a glass holder over strong sulphuric acid.

The holder, *A*, was attached to the palladium absorption apparatus as shown in Fig. 1 (p. 1045). The central portion of the apparatus consisted of a series of three glass bulbs, *B*, each of about 50 c.c. capacity, containing some 10 grams of freshly reduced palladium black, previously heated to redness in a vacuum. The tube leading from the bulbs was at one end twice bent at right angles, and sealed to a glass capillary tap, *a*, on the other side of which was a T joint, *b*, the latter serving to connect the bulbs through its vertical branch with the gas holder, *A*, and through its horizontal branch with the laboratory vessel, *C*, standing over mercury in a wooden trough, *D*. The tube leading from the other end of the bulbs after being bent at right angles was sealed to the glass capillary tap, *c*, through which a connection was made by means of a glass capillary tube with a manometer, *E*, standing over mercury in the same glass reservoir as the barometer, *F*, and also with the Sprengel pump, *H*, by means of which any gas in *B* could be drawn off and collected in tubes over mercury in the trough, *K*. The absorption bulbs, *B*, were immersed in a rectangular tin trough, *L*, containing water, so that they could be maintained at any temperature between

that of the room and 100°, as circumstances required. There were only two rubber joints in the whole apparatus, namely, those connecting the holder, *A*, and the laboratory vessel, *C*, with the branches of the T piece leading to the tap, *A*, of the absorption apparatus. These two joints were made of stout pump tubing firmly wired at either end to the glass tubes which they served to connect.

At the outset of an experiment, the taps, *a* and *c*, of the absorption bulbs and *e*, of the laboratory vessel, *C*, were opened and the whole apparatus, with the exception of the holder, *A*, was thoroughly ex

FIG. 1.



The palladium absorption apparatus.

hausted by means of the Sprengel pump, *H*. The tap *e* was then closed, the pump stopped, and by opening tap *d* of the gas holder, *A*, a quantity of the gas under examination was drawn over into *B*, until the level of the mercury in the manometer, *E*, had fallen within a few mm. of that in the vessel, *G*. The taps *d* and *a* were then closed, and the progress of the absorption of the hydrogen by the palladium in *B* could be followed by observing from time to time the mercury level in *E*. In about 20 minutes, the absorption had ceased, and the residual gas was drawn off by the Sprengel pump into tubes standing over mercury in the trough, *K*.

The water in the bath, *L*, was now heated to the boiling point, when much of the gas absorbed by the palladium during the previous operation was liberated and drawn off through the pump. Finally, the bulbs were exhausted at 100° and cooled to the ordinary temperature to be ready for the next absorption. These processes were repeated until the whole of the gas in *A*, usually about 3 litres, had been passed through the absorption bulbs and reduced to about 400—500 c.c. (first residue). This first residue was then introduced in three or four portions into the laboratory vessel, *C*, and subjected to a second concentration in the same manner as before, when its volume was usually reduced to about 120—150 c.c. (second residue). This gas still contained hydrogen, and, indeed, it is impossible to eliminate all the hydrogen from such a mixture of gases by a process of absorption with palladium, as the hydrogen in palladium hydride has an appreciable vapour pressure, even at the ordinary temperature. The last traces must be oxidised and removed as water by contact with "oxidised" palladium.

After this second concentration, therefore, the absorption bulbs were detached from the apparatus, the palladium black taken out and heated to dull redness in a hard glass tube attached to a Sprengel pump until as much as possible of the occluded hydrogen had been removed. The pump was then detached, and the palladium maintained at a red heat in a gentle current of air until it had acquired the characteristic dark blue oxidation tint. The "oxidised" palladium, after being cooled, was transferred again to the absorption bulbs, which were then sealed on to the apparatus, and the whole exhausted as before. The residual gas from the second concentration was introduced into *C*, and drawn over into the bulbs by momentarily opening taps *e* and *a*. The water in the bath, *L*, was heated to the boiling point, and the gas allowed to remain in the bulbs at this temperature for 20 minutes or half an hour, after which the bulbs were allowed to cool, and the residual gas was drawn off through the pump into tubes standing over mercury and each containing a small piece of solid caustic potash. The residual gas so obtained from each of the three different experiments was analysed by exploding a measured volume of it with excess of oxygen, in some cases diluted with air free from carbon dioxide, and determining (1) the 'contraction' (*C*) on explosion; (2) the 'absorption' (*A*) which occurred when the products of explosion were treated with potassium hydroxide, and (3) the oxygen (*X*) used up in the explosion.*

* All gas analyses involved in this research were carried out by means of an improved form of McLeod apparatus designed by one of us, and described at a former meeting of the Society (Proc., 1898, **14**, 154); we have found that this apparatus is especially adapted to the accurate analysis of hydrocarbon mixtures. The '*volumes*' quoted in the text are deduced from the tensions of the moist gases in mm. of

The results are tabulated as follows :

Experiment.	A.	B.		C.	
		(i)	(ii)	(i)	(ii)
Volume of gas taken	65·3	40·3	136·0	100·0	121·5
,, oxygen added	154·3	66·4	389·0	249·75	175·2
,, air added	nil	—	nil	196·65	232·1
Volume after explosion	152·0	150·8	406·8	386·2	431·5
,, treatment with KOH..	119·3	133·1	346·0	355·4	383·6
,, treatment with alkaline pyrogallol	—	102·2	178·0	—	—
Contraction (C)	67·3	35·6	118·2	60·2	97·3
Absorption (A)	32·7	17·7	60·8	30·8	47·9
Oxygen (X)	—	35·5	121·0	—	97·05
Ratio, C/A	2·07	2·01	1·94	1·96	2·03
Ratio, C/X	—	1·0	0·98	—	1·0

There can be no doubt that the hydrocarbon in these mixtures was in each case methane and methane only, for

Methane requires	C/A 2·0	and	C/X 1·00.
Ethane ,,	1·25 ,,		0·71.
Propane ,,	1·00 ,,		0·60.

B. Examination of the Gas obtained in the Arc Experiments.

Our earlier experiments had shown that, in addition to acetylene, saturated hydrocarbons are formed by the direct union of carbon and hydrogen at the temperature of the electric arc. It was necessary to ensure the complete removal of this acetylene and any other unsaturated hydrocarbons, as well as of the hydrogen, before attempting to identify the residual saturated hydrocarbon.

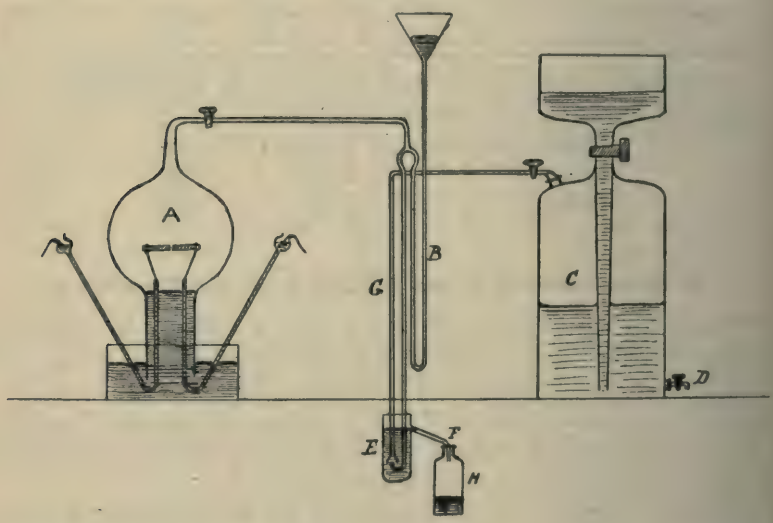
As a fairly large volume of this residual gas was ultimately required, and as it was desirable to determine whether the character and composition of the saturated hydrocarbon in any way depended upon the time during which the arc was maintained, the gas obtained in five different experiments was investigated. Each experiment was carried out in the arc apparatus as described in our previous paper (pp. 52—57), except that no samples of gas were collected during the time the arc was being passed, which varied from 10 minutes to an hour in the different experiments.

As soon as the arc apparatus, *A*, had cooled, the products were drawn off by means of the Sprengel pump, *B* (see Fig. 2, p. 1048), and sent

mercury when brought to a certain constant volume, at a constant temperature, in the measuring vessel of the instrument, the 'vacuum' in the barometer being always kept saturated with water vapour.

forward by means of a special device under a pressure of 2—3 mm. of mercury into the glass gas holder, *C*, previously filled with an ammoniacal solution of cuprous chloride. The solution so displaced was allowed to run away through the glass tap, *D*, into a large Winchester quart bottle. The device for drawing off the gas from *A* through the pump and sending it forward under pressure to *C*, consisted in immersing the delivery tube of the Sprengel in a large test-tube, *E*, three-quarters full of mercury, to which a side tube, *F*, had been fused. Over this delivery tube was fixed the funnel-shaped end of a vertical glass tube, *G*, the other end of which was attached to the tube leading into the holder, *C*. The mercury flowing over from the pump ran off through the side tube, *F*, into the bottle, *H*. The capacity of the gas holder, *C*,

Fig. 2.



was about half as large again as that of the globe of the arc apparatus, so that after the products had been all collected in *C*, it still remained about one-third full of the ammoniacal cuprous chloride solution. The gas was allowed to remain in *C* for at least two days, to ensure the complete absorption of acetylene and any trace of carbon monoxide, and was then transferred to another similar gas holder, previously filled with strong sulphuric acid, over which it was allowed to stand for other three or four days. The gas could now only consist of hydrogen, saturated hydrocarbons, and any nitrogen originally contained in the hydrogen. The gas holder was therefore attached to the palladium absorption apparatus for the removal of hydrogen, and treated as was the gas from the tube experiment (see p. 1044).

The residual mixture of hydrocarbons and nitrogen was analysed by mixing a measured volume of it with excess of oxygen, diluted in some cases with air free from carbon dioxide and measuring (1) the contraction, C, on explosion; (2) the absorption, A, which occurred when the products were treated with caustic potash. In certain cases, the oxygen used in the combustion of the hydrocarbons was also determined.

(1) *Blank Experiment.*—In order to test the purity of the hydrogen used in these experiments and the validity of the method employed, a blank experiment was performed in which hydrogen prepared and purified as described in our previous paper (p. 45) was passed into the arc apparatus, and without the arc having been formed, was then transferred by means of the Sprengel pump, *B* (Fig. 2), to the holder containing the ammoniacal cuprous chloride solution. From thence it was passed into a holder containing strong sulphuric acid, and afterwards subjected to the action of palladium in the absorption bulbs. The only differences between this blank and a real arc experiment were as follows. (1) A small quantity of nitrogen was allowed to mix with the hydrogen before it passed into the arc apparatus, in order that there might be a measurable residue for analysis after hydrogen had been removed in the final stages. (2) The arc was not formed, and (3) the final treatment of the gas with "oxidised" palladium at 100° was omitted.

As nearly as possible 2 litres of hydrogen were passed into the globe of the arc apparatus; after two "concentrations" in the palladium absorption apparatus it was reduced to about 80 c.c.

This residue was exploded in the gas analysis apparatus with measured volumes of pure hydrogen prepared by the electrolysis of water, and subsequently purified by means of palladium, and of air free from carbon dioxide. The products of explosion were afterwards treated with caustic potash, when a very slight absorption occurred. The details of the analysis are as follows:

Volume of residual gas taken	84·9
„ hydrogen added	57·1
„ air „	205·1
„ after explosion	262·6
„ after treatment with KOH	262·3

Contraction, C = 86·7. Absorption, A = 0·3.

Assuming that this small absorption was due to carbon dioxide formed by the combustion of methane originally present in the 2 litres of hydrogen used, it follows that this impurity did not exceed 0·015 per cent. by volume. We may therefore assume that the hydrogen used for the experiments recorded in this paper was practically free from

hydrocarbon impurity. Further, since the observed contraction is very little more than the sum of the contraction required by the hydrogen added (85·7) and the methane (0·6) present, this blank experiment indicates that practically the whole of the original hydrogen used had been removed by the palladium black. It was, however, deemed advisable not to omit the final treatment with "oxidised" palladium in the actual experiments.

(2) *Actual Experiments.*—The arc apparatus was in each case about two-thirds filled with hydrogen (about 2 litres), and the arc (voltage = 160) maintained for a period varying from 10 minutes to an hour in the different experiments. After removal of acetylene and hydrogen in the manner already described, the residual gas was analysed by explosion with excess of oxygen in the usual manner.

The details of each experiment, and the analytical results are given in the following table:

Experiment.	I.	II.	III.	IV.	V.
Time during which arc was maintained	10 mins.	30 mins.	30 mins.	1 hour	1 hour
Volume of residual gas after removal of acetylene and hydrogen	40 c.c.	—	60 c.c.	60 c.c.	75 c.c.*
Volume of residual gas after deducting nitrogen	35 c.c.	—	54 c.c.	50 c.c.	45 c.c.
Volume of gas taken	60·9	36·1	55·7	62·7	74·2
,, oxygen added	510·9	330·0	443·3	528·4	482·2
Volume after explosion	456·2	315·1	388·0	476·6	462·2
,, treatment with KOH	382·9	284·2	318·0	405·2	402·7
Contraction (C)	115·6	51·0	111·0	114·5	94·2
Absorption (A)	73·3	30·9	70·0	71·4	59·5
Ratio, C/A	1·58	1·65	1·58	1·62	1·58

* The large amount of nitrogen in this residual gas was due to an accidental in-leakage of air during the final absorption of hydrogen by means of oxidised palladium.

These experiments prove beyond all possible doubt that hydrocarbons of the methane series are produced when the electric arc is made between carbon terminals in an atmosphere of hydrogen. The actual quantity of these saturated hydrocarbons so formed is to some extent dependent upon the time during which the arc is maintained, attaining a maximum, as our earlier experiments showed, after about half an hour, and afterwards remaining fairly constant (see also previous paper, pp. 57—58). Further, it is a remarkable fact that the ratio C/A found on exploding the residual saturated hydrocarbons with excess of oxygen is practically constant (1·6) and independent of the time during which the arc is

maintained. It may therefore be concluded that whatever may be the number and composition of the saturated hydrocarbons obtained in a given experiment they are formed simultaneously, and at equal rates throughout.

The experiments indicate, moreover, that methane is one of the saturated hydrocarbons as the ratio $C/A = 1{\cdot}6$ could only be given by a mixture of saturated hydrocarbons containing methane (p. 1047).

The analytical numbers, however, afford no clue as to either the character or the number of the other saturated hydrocarbons. For example, the results obtained in the case of the residual gas from experiment I would be given by any one of the following mixtures :

(1).		(2).		(3).	
CH_4.....	52·5	CH_4 ...	69·5	CH_4 ...	75·1 per cent.
C_2H_6 ...	34·0	C_3H_8 ...	16·9	C_4H_{10} ...	11·3 ,,
*N_2	13·5	N_2	13·6	N_2	13·6 ,,
	100·0		100·0		100·0

or, indeed, by an unlimited number of other mixtures of nitrogen methane, and one or more other saturated hydrocarbons. Further, since the densities of all such possible mixtures are identical, it was not possible to distinguish between the various interpretations of the chemical analysis by means of a density determination. With the view, however, simply of checking the chemical analysis, the density of the residual gas obtained in experiment II, referred to hydrogen, was determined ; it was found to be 11·7 instead of 11·4 as calculated from the analysis.

C. Diffusion Experiments with the Residual Gas from the Arc Experiments.

It was now necessary to obtain some evidence as to the character of the saturated hydrocarbons other than methane formed in the arc experiments. It seemed probable that one or other, if not both, of two methods would enable us to settle the question. The first method consisted in subjecting some of the residual gas from the arc experiments to a slow process of diffusion through porous clay tubes many times repeated, and comparing its behaviour with that of artificial mixtures of methane and nitrogen with other saturated hydrocarbons (ethane, propane, &c.) giving the same analytical results. The other method, which the kindness of Professor Ramsay enabled us to carry out, consisted in liquefying the hydrocarbons in the residual gas from

* Results for nitrogen given in this paper are all calculated ' by difference.'

the arc experiments, and subsequently fractionally distilling the liquid. For the purpose of the diffusion experiments, we mixed together

30 c.c.	of residual gas from experiment	I.
45	„	III.
45	„	IV.
Total 120 c.c.		

The percentage composition of this mixture, according to analysis, is shown below, supposing that there are only two saturated hydrocarbons present, and that the second is (1) ethane, (2) propane, and (3) butane.

(1).		(2).		(3).	
CH_4.....	54·3	CH_4 ...	70·7	CH_4 ...	76·2 per cent.
C_2H_6 ...	32·8	C_3H_8 ...	16·4	C_4H_{10} ...	10·9 „
N_2	12·9	N_2	12·9	N_2	12·9 „

The relative ratio at which the constituents of such mixtures would diffuse through a porous plug can, of course, be calculated from their densities and partial pressures; taking the rate for the methane in each case as unit, the rates for the other constituents are as follows:

	(1).	(2).	(3).
Ethane	0·441	—	—
Propane	—	0·139	—
Butane	—	—	0·074
Nitrogen.....	0·18	0·133	0·128

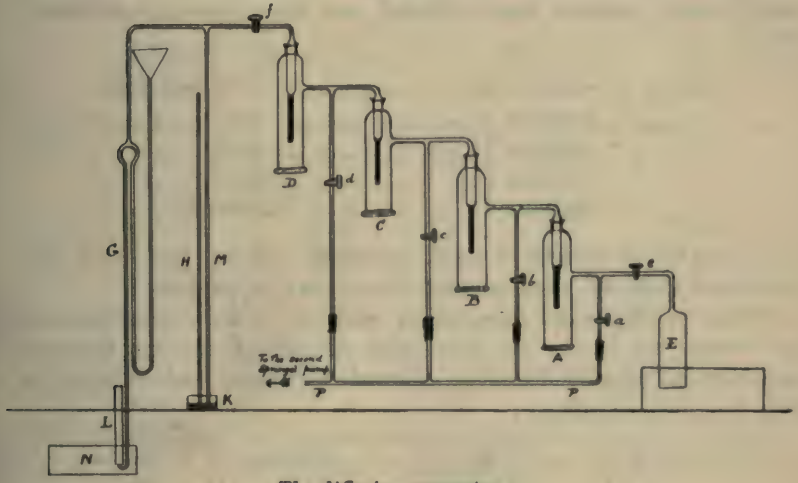
Diffusion Apparatus (see Fig. 3, p. 1053).—This consisted of four glass gas wash-bottles, *A*, *B*, *C*, *D*, arranged in series, as shown in the diagram. The central wide glass tube, which fitted into the neck of each bottle by a ground glass joint, was drawn out in the blow-pipe flame and then cut off about an inch below the joint. To it was attached a piece of clay pipe stem about 3—4 inches long, closed at the bottom in the oxyhydrogen flame. The four bottles were connected by fused glass joints, and between each pair was inserted a glass T joint terminating in a glass stopcock (*b*, *c*, *d*). The bottle, *A*, was connected by means of fused glass joints through a similar T piece with the laboratory vessel, *E*, standing in a wooden trough over mercury. The fourth bottle, *D*, was connected also by means of fused glass joints with a T piece leading through its vertical branch to the manometer, *M*, and through its horizontal branch to the Sprengel pump, *G*. *H* is a barometer standing in the same mercury reservoir, *K*, and attached to the same millimetre scale as the manometer, *M*.

The vertical branches of the T pieces between the bottles, and be-

tween *A* and *E*, were continued downwards beyond the stopcocks, *a*, *b*, *c*, *d*, through joints made of stout india-rubber pump tubing* to a horizontal glass tube, *PP*, which led to a second Sprengel pump (not shown in the diagram), with its barometer and manometer. This second Sprengel pump served to exhaust the apparatus at the outset of a diffusion experiment, and at the finish to collect the last fraction. All other fractions were drawn off through the first Sprengel, *G*, and collected in tubes, *L*, standing in the trough, *N*.

At the outset of an experiment, the whole apparatus was exhausted by opening all the stop-cocks, *a*, *b*, *c*, *d*, *e*, and *f*, leading to the two pumps. As soon as the laboratory vessel, *E*, was full of mercury, the stopcock, *e*, was shut. Finally, when the exhaustion was complete,

FIG. 3.



The diffusion apparatus.

stopcocks, *a*, *b*, *c*, and *d*, leading to the second pump, were closed. The apparatus was now allowed to stand for 24 hours, to see whether the ground glass joints at the top of the four diffusion bottles, *A*, *B*, *C*, and *D*, were quite air-tight. It was found possible to make them so by pouring melted paraffin wax over the outer surface of each joint when the apparatus was exhausted.

The gas to be diffused was introduced into the laboratory vessel, *E*, and then by opening the stopcock, *e*, it was drawn over into the first diffusion bottle, *A*. The diffusion process at once began, and the various

* With the exception of these four joints, which were shut off from the bottles throughout the diffusion operations, and the four ground glass joints of the bottles, all other joints in the apparatus were of fused glass.

fractions, excepting only the final fraction, were collected through the first Sprengel pump, *G*. Finally, the stopcocks *a*, *b*, *c*, *d* were opened, and the residual gas, that is, the last fraction, was drawn off through the second Sprengel pump. It will therefore be clear that in each diffusion operation the gas passed through four porous plugs. The amount of gas taken for each "fractionation" varied within very wide limits. Usually, it amounted to between 25 and 120 c.c., and the time required for each operation varied from 9—18 hours, being shorter the larger the amount of gas involved.

Diffusion of a Mixture of equal Volumes of Methane and Oxygen in the Apparatus.—To obtain some idea of the efficiency of the apparatus, 100 c.c. of a mixture of equal volumes of methane and oxygen (oxygen has nearly the same density as ethane, which is, next to methane, the lightest saturated hydrocarbon) were slowly fractionated. Four nearly equal fractions were collected, and the oxygen in each determined.

Oxygen in original gas	.....	50·0 per cent.
„ fraction I	.....	42·5 „
„ fraction II	.....	52·0 „
„ fraction III	.....	58·5 „
„ fraction IV	.....	59·0 „

Twenty c.c. of fraction I were rediffused, and the first 5 c.c. collected and analysed. It contained 30 per cent. of oxygen.

Scheme of Diffusion Experiments with Arc Gases.—One hundred and twenty c.c. of the arc gases were introduced into the diffusion apparatus as already described, allowed to diffuse, and collected in four fractions, as follows:

Fraction A = 30 c.c.	Fraction C = 40 c.c.
„ B = 30	„ D = 20

Fraction C was then rediffused, the first 5 c.c. collected were added to A, the next 13 c.c. to B, and the residual gas collected separately. (Fraction C′.)

Fraction B was then rediffused. The first 15 c.c. were added to A, the next 14 c.c. to C′, and the residue to D.

At this stage, therefore, we had

Fraction A = 50 c.c. Fraction C′ = 36 c.c. Fraction D = 34 c.c.

Fraction A was diffused, and collected in two fractions.

Fraction A′ = 25 c.c. Fraction A″ = 25 c.c.

Fraction A′ was finally diffused and collected in three approximately equal fractions, *a*, *b*, and *c*.

Fraction D was diffused, and collected in two fractions.

Fraction D′ = 10 c.c. Fraction D″ = 24 c.c.

Fraction D″ was finally diffused and collected in three approximately equal fractions, *x*, *y*, and *z*.

The fractions *a* and *z* were analysed by exploding a measured volume of each with an excess of oxygen, and determining (1) the contraction, C, and (2) the absorption, A, as in previous analyses of the arc gases.

	Fraction *a*.	Fraction *z*.
Volume of gas taken	53·5	81·9
,, oxygen added	452·0	450·95
,, after explosion	405·8	380·1
,, ,, treatment with KOH	349·2	275·9
Contraction (C)	99·7	152·75
Absorption (A)	56·6	104·2
Ratio C/A	1·76	1·46

The composition of the fractions, assuming that the second hydrocarbon is (1) ethane, (2) propane, must be as follows:

Fraction *a*.		Fraction *z*.	
(1)	(2)	(1)	(2)
CH_4 = 72·0	CH_4 = 80·6	CH_4 = 36·6	CH_4 = 59·3
C_2H_6 = 16·8	C_3H_8 = 8·4	C_2H_6 = 45·3	C_3H_8 = 22·6
N_2 = 11·2	N_2 = 11·0	N_2 = 18·1	N_2 = 18·1
$\frac{\text{Methane}}{\text{Ethane}} = 4·29.$	$\frac{\text{Methane}}{\text{Propane}} = 9·6.$	$\frac{\text{Methane}}{\text{Ethane}} = 0·808.$	$\frac{\text{Methane}}{\text{Propane}} = 2·624.$

The ratios of the two hydrocarbons are important in view of the result of the two following experiments, in which artificial mixtures were diffused.

Diffusion of a Mixture of Methane, Ethane, and Nitrogen.—A mixture of methane, ethane, and nitrogen was prepared as nearly as possible of the same composition as that of the residual gas from the arc experiments, assuming that the second hydrocarbon was ethane.

The methane* employed was prepared by the action of a mercury-aluminium couple on a mixture of methyl iodide and methyl alcohol, and in order to remove any traces of hydrogen it might contain, the gas was passed over oxidised palladium sponge heated at 100°.

The ethane* used was prepared by decomposing zinc ethyl with

* The purity of both the methane and ethane (as well as of the propane used in the next experiment) was in each case proved by a careful analysis (explosion method), the details of which it is not necessary to record. The ratio C/A for the methane was found to be 2·0, and for the ethane 1·254.

water, and the nitrogen by passing a slow current of air over red-hot copper turnings until the whole of the oxygen had been removed.

The gases were then mixed in a small graduated holder over mercury. On analysis, the mixture was found to have the following percentage composition:

Methane = 51·77; ethane = 33·15; nitrogen (by difference) = 15·18, with ratio C/A = 1·575.

One hundred and twenty c.c. of this mixture were subjected to a precisely similar series of fractional diffusions as have been described in the case of the residual gas from the arc experiments, and finally the fractions *a* and *z* so obtained were analysed, with the following results:

	Fraction *a*.	Fraction *z*.
Volume of gas taken	49·2	45·0
„ oxygen added	483·95	440·0
Volume after explosion	445·4	407·2
„ treatment with KOH	395·9	354·3
Contraction (C)	87·75	77·8
Absorption (A)	49·5	52·9
Ratio C/A	1·77	1·47

The behaviour of the mixture of methane, ethane, and nitrogen when subjected to the process of fractional diffusion was similar to that of the residual gas from the arc experiment. The percentage composition of the two fractions *a* and *z* were therefore:

	a.	*z*.
Methane	70·1	34·7
Ethane	15·2	41·5
Nitrogen (by difference)	14·7	25·8
Ratio $\frac{\text{Methane}}{\text{Ethane}}$	4·62	0·835

Diffusion of a Mixture of Methane, Propane, and Nitrogen.—The propane used in this experiment was prepared by the action of sodium amalgam on a solution of *iso*propyl iodide in ethyl alcohol; analysis showed it to be pure (ratio C/A = 0·997). The three gases were mixed in a graduated holder over mercury; on analysis, the mixture was found to have the following percentage composition:

Methane = 65·5; propane = 17·65; nitrogen (by difference) = 16·85, with ratio C/A = 1·55, which is nearly that of the residual arc gases, assuming for the moment that the second hydrocarbon was propane. The mixture was subjected to a process of diffusion precisely similar to that carried out with the residual arc gases, and with the mixture of methane, ethane, and nitrogen.

This mixture seemed to behave differently during the diffusion

operations from either the arc gases or the mixture of methane, ethane, and nitrogen. The 'heavier' fractions passed through the apparatus much more slowly, and the final fractions were only pumped out with great difficulty; last traces of propane obstinately clung to the plugs, and were probably never removed. The fractions *a* and *z* were finally analysed, with the following results:

	Fraction *a*.	Fraction *z*.
Volume of gas taken	42·1	55·3
„ oxygen added	388·9	494·3
Volume after explosion	357·85	466·7
„ treatment with KOH	318·70	408·0
Contraction (C)	73·15	82·9
Absorption (A)	39·15	58·7
Ratio C/A	1·86	1·41

The percentage composition of these fractions would therefore be:

	a.	*z*.
Methane	80·80	43·8
Propane	4·09	20·8
Nitrogen	15·11	35·4

and the ratios $\frac{\text{methane}}{\text{propane}}$ are 19·75 and 2·10 respectively.

The results of these diffusion experiments are most easily understood if the ratio $\frac{\text{methane}}{\text{other hydrocarbon}}$ for the lightest and heaviest fractions obtained by the diffusion of the two mixtures of known composition be compared with the same ratio for the corresponding fractions obtained when the arc gases are subjected to the same process.

Mixture, CH_4, C_2H_6, N_2.			Mixture, CH_4, C_3H_8, N_2.		Arc gases.			
	Fraction.		Fraction.		(1) If ethane is present. Fraction.		(2) If propane is present. Fraction.	
	a	*z*	*a*	*z*	*a*	*z*	*a*	*z*
$\frac{\text{Methane}}{\text{Other hydrocarbon}}$	4·62	0·836	19·75	2·10	4·29	0·808	9·6	2·624
$\frac{R_a}{R_z}$	$\frac{4·62}{0·836} = 5·53$		$\frac{19·75}{2·10} = 9·4$		$\frac{4·29}{0·808} = 5·3$		$\frac{9·6}{2·624} = 3·6$	

The similarity between the results obtained with the artificial

mixture containing ethane and the residual gas from the arc experiment is so great that very little doubt can remain as to the presence of ethane in the arc gases. The similarity is especially brought out by comparison of the ratio R_a/R_z. In the two cases quoted, the ratios are almost identical, namely, 5·53 and 5·3, whereas if we assume the second hydrocarbon in the arc gases to be propane, we find $R_a/R_z = 3·6$, whilst for the artificial mixture containing propane the value 9·4 is obtained.

The evidence afforded by the diffusion experiments is therefore much more in favour of the supposition that the second hydrocarbon in the arc gases was ethane than that it was propane. On the other hand, it does not exclude the possibility of the gases having contained some small amount of propane in addition to methane and ethane.

D. Liquefaction and subsequent Fractional Distillation of the Hydrocarbons in the Arc Gases.

The idea of separating the hydrocarbons contained in the arc gases by a process of liquefaction and subsequent fractional distillation occurred to us at an early stage of our work, indeed before the diffusion experiments were seriously contemplated. We, however, had no means of carrying out the idea until Professor Ramsay, hearing of our difficulty, kindly offered to help us, and we desire to express our best thanks to him for his goodness in enabling us to bring our investigation to a satisfactory conclusion.

The following table of boiling points, expressed in degrees absolute, shows that there is a greater difference between the boiling points of methane and ethane than between those of benzene and the xylenes, and as a difference of so many degrees at so low a temperature means relatively much more than a similar difference at higher temperatures, the prospect of almost completely separating methane and ethane seemed good:

	Boiling points.	Diff.
Nitrogen.....	79°	
		>34°
Methane.....	113	
		>67
Ethane	180	
		>48
Propane	228	
		>46
Butane	274	

	Boiling points.	Diff.
Benzene.....	353·4°	
		>29·9
Toluene	383·3	
		>31·7
Xylenes...	411 to 415	
		61·6

About 100 c.c. of various fractions of the arc gases left over from the diffusion experiments were thoroughly mixed in a small holder over mercury; a portion of the mixture was analysed with the following results:

Volume of gas taken	38·5
„ oxygen added	344·3
Volume after explosion	312·25
„ treatment with KOH	268·25

Contraction (C) = 70·55. Absorption (A) = 44·00.

Ratio C/A = 1·60.

The gas would therefore have the following percentage composition, assuming (1) that the second hydrocarbon is ethane, (2) that it is propane:

(1)		(2)	
Methane	54·0	Methane	69·0
Ethane	30·0	Propane	15·0
Nitrogen	16·0	Nitrogen	16·0

It will further be noticed that this was practically the composition of the original arc gases before diffusion.

About 70 c.c. of this mixture were sealed up in an exhausted bulb, and forwarded to Professor Ramsay, who carried out the fractionation for us in the laboratory of the University College, London, as follows. The gas was passed into a small gas bulb immersed in boiling liquid air; a large portion of it solidified as white, snow-like crystals on the inner surface of the bulb, whilst another portion either liquefied or formed a vitreous, glassy solid. A third constituent, namely the nitrogen, which was only liquefied under pressure, was allowed to pass off uncondensed. The contents of the bulb were slowly volatilised and collected over mercury in three as nearly as possible equal fractions, A, B, and C, of about 20 c.c. each. The crystalline solid (the methane) disappeared during the early stages of the process, and the liquid or vitreous solid was entirely converted into gas at a very low temperature, certainly much below the boiling point of butane, and probably that of propane also. After the third fraction had been collected, there remained no residuum of gas in the apparatus. From the behaviour of the gas during the process, Professor Ramsay concluded that it certainly contained no butane, and that the second hydrocarbon was more probably ethane than propane.

Fraction A was found, on analysis, to consist of methane with some 15 per cent. of nitrogen, as the following figures indicate:

Volume of gas taken	49·80
„ oxygen added	124·90
„ air added (oxygen = 76·37)	364·35
Volume after explosion	455·0
„ treatment with KOH	412·9
„ treatment with alkaline pyrogallol	296·1
Oxygen used (124·9 + 76·37 − 116·8)	84·47

Contraction (C) = 84·05. Absorption (A) = 42·10.
Ratio C/A = 2.

The gas therefore had the percentage composition

Methane = 84·5.
Nitrogen = 15·5.

Fraction B on analysis gave the following numbers:

Volume of gas taken	38·0
„ oxygen added	99·8
„ air added (oxygen = 77·7)	370·5
Volume after explosion	432·5
„ treatment with KOH.....	390·9
„ treatment with alkaline pyrogallol	295·5
Oxygen used (99·8 × 0·988 + 77·7 − 95·4).....	80·9

Contraction (C) = 75·8. Absorption (A) = 41·6.
Ratio C/A = 1·82.

The gas evidently therefore contained a large quantity of methane with some ethane or propane and also nitrogen. Its percentage composition would be as follows, assuming (1) that the second hydrocarbon was ethane, (2) that it was propane:

(1)		(2)	
Methane	83·53	Methane	90·0
Ethane	12·97	Propane.....	6·5
Nitrogen.....	3·50	Nitrogen.....	3·5

The amount of oxygen actually used in the explosion agrees very closely with the 80·73 vols. required by 38 vols of either of the foregoing mixtures, if we allow for the fact that the oxygen added was found on analysis to contain 1·2 per cent. of nitrogen.

Fraction C, on analysis, yielded numbers agreeing very closely with those required on the supposition that it consisted of nearly pure ethane:

Volume of gas taken	32·7
„ oxygen added.....	483·0
Volume after explosion	435·0
„ treatment with KOH	372·0

Contraction (C) = 80·7. Absorption (A) = 63·0.
Ratio C/A = 1·28.

Now pure ethane requires C/A = 1·25. It is evident therefore that this fraction either consisted of ethane with a small quantity of methane, or that it contained nearly equal volumes of methane and

propane. There was evidently no nitrogen present, as the following figures indicate :

Methane = 2·6 (7·92 per cent.)	Methane = 17·7 (54·0 per cent.)
Ethane = 30·2 (92·07 „)	Propane = 15·1 (46·0 „)
32·8	32·8

The percentage composition of the *three* fractions would be as follows, (1) on the supposition that the second hydrocarbon was ethane, (2) that it was propane :

		A.	B.	C.
(1)	Methane	84·5	83·53	7·92
	Ethane	nil	12·97	92·07
	Nitrogen	15·5	3·50	nil
(2)	Methane	84·5	90·0	54·0
	Propane	nil	6·5	46·0
	Nitrogen	15·5	3·5	nil

The composition of the middle fraction, B, almost excludes the supposition that the second hydrocarbon was propane, for if it were so, the second series of figures would indicate that whereas we had completely separated nitrogen and methane whose boiling points differ by only 34°, we had not effected a separation of two hydrocarbons whose boiling points differ by as much as 115°.

To further test the matter, however, 10 c.c. of the fraction C were subjected to a process of diffusion in the apparatus we have described, which in one operation effected a considerable separation in a mixture of equal volumes of methane and oxygen (see page 1054).

If fraction C consisted of nearly equal volumes of methane and propane, we should expect to get a very considerable separation on diffusion ; on the other hand, if the gas was nearly pure ethane, on analysis very little difference should be found between the ratio C/A for the heaviest portion and 1·28, the ratio for the original gas diffused.

The 10 c.c. of gas were accordingly very slowly diffused through the apparatus, the operation extending altogether over 12 hours. The first 6·5 c.c. collected were rejected, and the last 3·5 c.c. were analysed, with the following results :

Volume of gas taken	27·95
„ oxygen added	488·35
Volume after explosion	450·9
„ treatment with KOH	398·5

Contraction (C) = 65·4. Absorption (A) = 52·4.
Ratio C/A = 1·25.

The result is, we are inclined to think, quite decisive. The evidence is overwhelmingly in favour of the view that the second saturated hydrocarbon formed when the electric arc is maintained between carbon terminals in an atmosphere of hydrogen is ethane.

Discussion of Results.

Our experiments prove that methane, the simplest of all hydrocarbons, is the first to be formed by the direct combination of its elements, for it alone is produced at the lower temperature of 1200° when the velocity of combination is just measurable. At some temperature, at present unknown, between 1200° and 3500° the temperature of the arc, acetylene, and ethane begin to be formed; in the arc the formation of all these hydrocarbons continues until a certain equilibrium between them and carbon vapour and hydrogen is established. Calculating from the results of our earlier experiments, interpreted in the light of our later work, we find that the proportions between the three hydrocarbons and hydrogen when this equilibrium is attained are somewhat as follows:

Hydrogen	90—91 per cent.
Acetylene	7— 8 „
Methane.....	1·25 „
Ethane	0·75 „

It is, of course, open to discussion whether acetylene and ethane are formed in the arc directly from their elements, or indirectly by the decomposition of methane. At first sight it may seem probable that methane is the first product of the combination of carbon vapour with hydrogen in the arc, as it undoubtedly is of the action of hydrogen upon solid carbon at 1200°. The fact, however, that methane and ethane are produced simultaneously, and at rates which bear a constant ratio to each other during the whole time the arc is maintained, indicates, we think, that ethane is formed directly from its elements, and not indirectly by the decomposition of either methane or acetylene. With regard to the acetylene, a study of the results recorded in our previous paper, particularly those of the arc experiments II and III, shows that its rate of formation bears a nearly constant ratio to the rates of formation of the other two hydrocarbons, and, further, that the quantity of it present at any given moment throughout an experiment is always far in excess of the proportions of the other two hydrocarbons, even when these are considerably below the 'equilibrium limits.' These considerations, we think, point to the conclusion that acetylene also is formed directly from its elements. It is, however, difficult to draw any hard and fast conclusions as to the character and sequence of the chemical changes which occur in the arc experiments.

Our results also open up the question of the stability of hydrocarbons at high temperatures. The recent publication of preliminary notices of work on the decomposition of various organic compounds, including some hydrocarbons, by W. Ipatieff (*Ber.*, 1901, 34, 596) and also by W. Löb (*Ber.*, 1901, 34, 915) make it desirable that we should now indicate the lines upon which we have been working on this subject for some months, in order that unnecessary overlapping may be prevented. If, as we have shown, methane is the only hydrocarbon to be formed at 1200° from its element, it is probable that it alone can permanently exist at this temperature; we are, therefore, investigating the decomposition of methane, ethane, ethylene, acetylene, and certain aromatic hydrocarbons at 1200° or thereabouts, and hope shortly to communicate some results to the Society.

We have much pleasure in expressing our indebtedness to Professor Dixon for valuable criticisms at various times during the course of the research, to Professor Ramsay for so kindly helping us in the separation of the saturated hydrocarbons obtained in the arc experiments, to Messrs. Johnson and Matthey for the loan of palladium required for the hydrogen absorptions, and finally to the Government Grant Committee of the Royal Society for repeated grants which have enabled us to purchase the special apparatus required for the research, including that used for the gas analyses involved.

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CX.—*On the Decomposition of Carbon Dioxide when submitted to Electric Discharge at Low Pressures.*

By J. Norman Collie, Ph.D., F.R.S.

During some experiments which were being made on the relative resistance of gases at low pressures in vacuum tubes to the passage of the electric spark, carbon dioxide was found to exhibit peculiarities. As these pointed to decomposition of the gas, the literature bearing on the subject was consulted, and as the evidence was conflicting, an inquiry into what occurred seemed necessary.

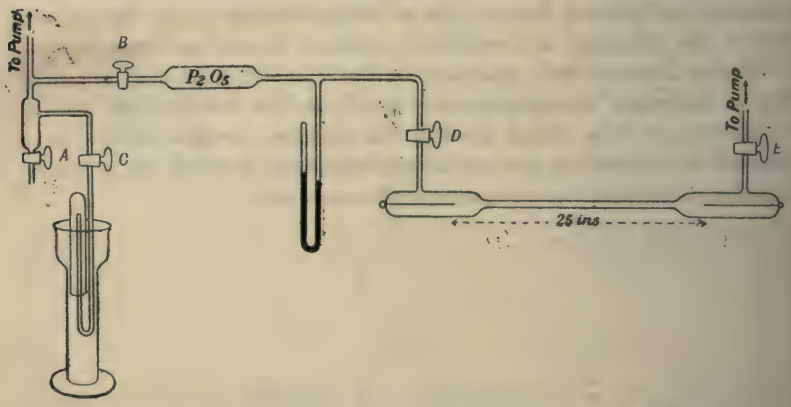
So far back as 1860, H. Buff and A. W. Hofmann (this Journal, 12, 282) noticed that at the ordinary pressure carbon dioxide underwent imperfect decomposition when subjected to the sparks from an induction coil. They say, "the spark traverses the gas with a violet light. In the commencement of the experiment, the expansion is very

appreciable; $7\frac{1}{2}$ c.c. of carbonic acid, after a few minutes, became $8\frac{3}{4}$ c.c.; but further decomposition proceeded with extreme slowness, until, after the lapse of half an hour, the accumulated carbonic oxide exploded with the liberated oxygen, when the original volume of the carbonic acid was restored, again to undergo a similar set of changes."

But in opposition to this, in a very comprehensive paper on the spectra of carbon compounds, Prof. A. Smithells (*Phil. Mag.*, 1901, [vi], **1**, 476) brings forward arguments for the stability of carbon dioxide when submitted to the electric discharge at the low pressure of a vacuum tube, although at the same time he points out that this idea is in opposition to the views which he takes with regard to the Swan spectrum being that of carbon monoxide.

As it did not seem difficult to obtain the gases from the interior of a vacuum tube in sufficient quantity for analysis, the following investigation was made.

The form of apparatus used was as follows:



The carbon dioxide could be introduced by means of the tap *C*, the gas entering into the space between the taps *A* and *D*. The pressure was read off on the gauge. The distance between the two electrodes, which were of stout aluminium, was 25 inches; the capillary tube joining the two ends of the vacuum tube was of 1 mm. bore.

Pure carbon dioxide, made by heating sodium hydrogen carbonate, was introduced into the tube in the ordinary manner and dried by passing over a layer of phosphoric oxide. Connected with the vacuum tube was a mercury gauge to measure the pressure of the gas. On the vacuum tube were two glass stopcocks, one at each end, so that during the sparking of the gas only that portion confined in the tube should be submitted to the discharge. Any gas, therefore, introduced into the vacuum tube after sparking could be directly pumped out by means of a Töpler pump and analysed.

A Newton-App coil and a couple of accumulators were used for the production of the electric discharge.

In the first set of preliminary experiments some of the pure carbon dioxide was sparked during a period of from 1 to 10 minutes under a pressure of 5 mm. It was found that the residual gas, when pumped out, was largely insoluble in caustic soda, and that the carbon dioxide, in amounts varying from 60—70 per cent., had been decomposed. This residual gas, when submitted to an electric spark under the ordinary pressure, exploded, and then was soluble (all except a small bubble) in caustic soda.

Large quantities were therefore experimented with in order to obtain a greater volume of the residual gas. This was effected by mixing the products from several experiments. As a result, it was found that, after being filled four times at 3 mm. pressure, and the contents sparked for 3 minutes, the tube yielded 2·2 c.c. of gas. 1·7 c.c. were left after treatment with caustic soda ; 0·5 c.c., therefore, of undecomposed carbon dioxide had been absorbed. On exploding the 1·7 c.c., it became almost entirely soluble in caustic soda. By calculation, the original volume of the carbon dioxide must have been 1·633 c.c., and of this 1·133 c.c. had been decomposed, which is equivalent to 69 per cent.

Several other experiments were made, and always with the same result, the amount of decomposition varying from 65—70 per cent.

In two of the above experiments, during the decomposition of the gas, the vacuum tube was in open connection with the mercury gauge, and the increase in pressure could be noticed even after the tube had been allowed to cool.

To test whether the aluminium electrodes were in any way instrumental in effecting the decomposition of the carbon dioxide, stout platinum ones were substituted for them, and at first very contradictory numbers were obtained. The gas was introduced at pressures varying from 2½ to 6 mm., and the sparking continued for 5 minutes in each case. The amount of carbon dioxide decomposed varied from 33 to 57 per cent.

During the passage of the current, however, it was noticed that flickerings occurred in the tube when the negative electrode became hot, and that the glow on the hot negative electrode changed from the livid blue exhibited by the mixture of decomposed gases to the purple colour which was characteristic when the gas was first subjected to the electric discharge, this seeming to indicate that recombination was taking place. Accordingly, the tube was again filled at 5 mm. pressure and sparked for 1 minute. On pumping out the gas, it was found that 65 per cent. had been decomposed into carbon monoxide and oxygen.

The tube was again filled at the same pressure, and subjected for

5 minutes to the same spark. A more powerful current was turned on till the platinum negative electrode became red hot; the flickerings were again noticed, and the colour of the incandescent gas at the hot platinum electrode changed as before to a purple colour. The current was stopped, and the gases analysed. Only 22 per cent. had been decomposed.

An electrodeless tube was next tried, and when it was filled at 5—6 mm. pressure and a strong current employed for 1 minute, it was found that no less than 50 per cent. of the carbon dioxide underwent decomposition into carbon monoxide and oxygen. In another experiment, which was carried on for 5 minutes, 62 per cent. of the gas was decomposed. These results show that carbon dioxide gas is undoubtedly decomposed to a large extent by the current, irrespective of the electrode employed.

Many more experiments were made with another tube in which one electrode was stout aluminium and the other a coiled piece of thin platinum wire. In every case, when the stout aluminium wire was the negative electrode and the tube was filled at pressures varying from 1—12 mm., 70 per cent. of the carbon dioxide was found to be decomposed after 1 to 2 minutes' sparking. The following experiment, however, is worth recording in detail.

The residual gas from several experiments, after all the carbon dioxide had been removed, was analysed. Part of it was found, on explosion, to yield nothing but carbon dioxide. Also, another part was reduced exactly one-third in volume by treatment with an alkaline solution of pyrogallol, and the remaining two-thirds was absorbed entirely by an ammoniacal solution of cuprous chloride. It was therefore a mixture of two volumes of carbon monoxide and one volume of oxygen.

Some of this gas was introduced in portions at 10 mm. pressure into the vacuum tube and sparked for 2 minutes, the aluminium being the negative electrode. After pumping out finally, 9·3 c.c. of residual gas were obtained. This volume was reduced to 7·6 c.c. when treated with caustic soda, showing that carbon dioxide had been formed, and that the mixture of carbon dioxide, carbon monoxide, and oxygen was in the same amount as if 74 per cent. of carbon dioxide had been decomposed.

The residual 7·6 c.c. of carbon monoxide and oxygen were next introduced into the tube in the same manner, but at a lower pressure, namely, 2 mm., in order that when the platinum electrode was made the negative pole it might be heated by the current. After pumping out, the 7·6 c.c. had decreased to 5·2 c.c. On treatment with caustic soda, only 0·6 c.c. remained, which proved to be pure carbon monoxide.

Thus, by merely varying the conditions of the experiment, carbon

dioxide had been first decomposed, to the extent of 70 per cent., into carbon monoxide and oxygen. Next, the carbon monoxide and oxygen alone, by the same treatment, partly recombined, forming carbon dioxide, but when a hot platinum electrode and increased current were employed, the carbon monoxide and oxygen combined almost completely to form carbon dioxide, in fact they would have probably done so entirely if, in the splashing of the platinum on to the side of the tube, a small amount of oxygen, 0·3 c.c., had not been occluded by the metal.

Carbon dioxide which had been dried in the pump for about 50 hours decomposed just as easily as undried gas passed straight into the tube, for some gas thus freed from aqueous vapour when sparked under 5 mm. pressure for one minute was found, on analysis, to have been decomposed to the extent of 65 per cent.

The following results show that the decomposition was fairly rapid. Carbon dioxide sparked under 10 mm., 3 mm., and 1 mm. pressure for only 10 seconds decomposed to the extent of 32, 55, and 63 per cent. respectively.

Carbon monoxide, however, seems to be far more stable. When subjected to the same treatment with an ordinarily powerful spark, the current may be left on for half an hour with no appreciable result; moreover, the gas gives no turbidity with baryta water. If, however, the current is sufficiently strong to make the negative electrode red hot, a very small amount of carbon dioxide is produced, too little to measure, but sufficiently great to cause a white precipitate with baryta water, and small specks of something black, presumably carbon, collect on the positive electrode.

Several experiments were made with mixtures of hydrogen and carbon dioxide in the hope that perhaps the carbon monoxide at the moment of its liberation from the carbon dioxide would unite with the hydrogen to produce formaldehyde; the presence of formaldehyde, however, could not be detected, but the decomposition in a mixture of nearly equal quantities of carbon dioxide and hydrogen was considerably retarded.

The residual gas was treated with caustic soda, ammoniacal cuprous chloride, and finally spongy palladium. There remained a very small quantity of gas. It could not have been ethylene for it was not altered by fuming sulphuric acid, but when mixed with oxygen it exploded feebly, and left a small quantity of gas soluble in caustic soda. Probably the gas was methane, but owing to the great difficulty in producing enough of it for analysis in a proper manner, the matter was left for the present. Moreover, the observation that carbon monoxide and hydrogen can be made to yield methane is not new, as Sir B. C. Brodie (*Proc. Roy. Soc.*, 1872, 21, 245) obtained 6 per cent. of this

gas by sparking a mixture of carbon monoxide and hydrogen in a Siemens' induction tube.

The fact, however, that carbon dioxide is capable of being decomposed to the extent of 65 per cent. in the space of 10 seconds, when it is subjected at low pressures to the electrical discharge from an ordinary induction coil, is of considerable interest, especially as it seems probable that the absorption of carbon dioxide by plants, and the subsequent liberation of oxygen when the plant is exposed to sunlight, may be due to this excessive instability of carbon dioxide when subjected to electrical strain. That heat vibrations have much to do with the decomposition seems improbable, and the severance of the oxygen in carbon dioxide from the compound both in a vacuum tube by electrical energy, and in the plant by agency of light, may possibly be due to the same cause. It would be interesting to know whether the amount of oxygen evolved by growing plants in sunlight is equivalent to about two-thirds of the carbon dioxide absorbed, as this seems to be the point of equilibrium reached in the vacuum tube during either the decomposition of carbon dioxide into carbon monoxide or the union of carbon monoxide and oxygen.

There has just appeared an interesting paper by Ciamician and Silber (*Ber.*, 1901, **34**, 1530), in which they show how light may play an important part in chemical action, especially in the case when coloured substances, such as quinone, are allowed to react with easily dehydrogenised compounds such as alcohol. The reaction of quinone with alcohol is as follows:

$$C_6H_4O_2 + C_2H_6O = C_6H_4(OH)_2 + C_2H_4O.$$

Many other carbonyl compounds were experimented with, and the same result obtained. The general reaction can be expressed thus:

$$:CO + \cdot OH = :C\cdot OH + :O.$$

Between this reaction and the assimilation of carbon dioxide in living plants which contain the coloured chlorophyll a close parallel can be drawn. The carbon dioxide, in presence of sunlight and the strongly coloured chlorophyll, breaks down into carbon monoxide (a free carbonyl group) and oxygen. This carbon monoxide then reacts with the water in an exactly similar manner to that given in the equation above,

$$:CO + H\cdot OH = H\cdot CHO + :O.$$

and formaldehyde or formic acid is produced—or perhaps combination of carbon with carbon may take place, as is the case, according to Ciamician and Silber, when acetophenone is mixed with alcohol and exposed to sunlight.

$$2COMePh + C_2H_6O = CMePh(OH)\cdot CMePh\cdot OH + C_2H_4O.$$

Carbon monoxide would first yield formaldehyde, H_2CO, which, in presence of water, chlorophyll, and sunlight, might yield glycolaldehyde,

$$2\begin{matrix}H\\H\end{matrix}\!>\!CO + H_2O = \begin{matrix}H\\H\end{matrix}\!>\!C(OH)\cdot CHO + H_2O,$$

and by polymeric condensation the glycolaldehyde would yield sugars.

RESEARCH LABORATORY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

CXI.—*Metal-Ammonia Compounds in Aqueous Solution. Part III. Salts of the Alkaline Earth Metals.*

By H. M. DAWSON and J. MCCRAE.

DRY calcium chloride forms with ammonia a complex salt, but we have no direct evidence that this complex is capable of existence in solution.

Raoult (*Ann. Chim. Phys.*, 1874, [v], 1, 263) has shown that the solubility of ammonia in concentrated calcium nitrate solution is greater than in pure water, and Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1899, 31, 985; *Chem. Centr.*, 1900, i, 938) has found that the partial pressure of ammonia over an ammoniacal solution of calcium chloride is less than that over a pure aqueous solution of the same concentration. Konowaloff's observation has been confirmed by Gaus (*Zeit. anorg. Chem.*, 1900, 25, 236). There is in these results an indication that the dissolved calcium salt (the calcium ion) is capable of fixing ammonia.

We have extended our experiments on the distribution of ammonia between aqueous salt solutions and chloroform to solutions containing salts of the alkaline earth metals. In our first communication (Trans., 1900, 77, 1250), we have given results with calcium chloride, but these are to be regarded as preliminary experiments.

The method of experimentation has already been sufficiently described (this vol., 495). The experiments were carried out at 20°, and the results given on p. 1070 have been obtained:

If these results are compared with those obtained for the salts of the alkalis on the one hand, and with the salts of copper, zinc, cadmium, and nickel on the other, it will be observed that, speaking generally, the salts of the alkaline earth metals occupy a position between these two groups. In general, the absorptive power of solutions of the alkali metal salts for ammonia is less than that of pure

Strength of aqueous solution. n.	Concentration of NH_3 in the aqueous part, grams per litre. c_1.	Concentration of NH_3 in the $CHCl_3$, gram per litre. c_2.	Coefficient, $\frac{c_1}{c_2}$. k'.	Coefficient for pure water when concentration of NH_3 in $CHCl_3$ is c_2. k.	$\frac{k-k'}{n}$.
Calcium chloride:					
1·0	8·525	0·3031	28·13	26·24	−1·89
0·8	8·574	0·3090	27·74	26·23	−1·89
0·4	8·534	0·3152	27·97	26·22	−2·12
0·2	8·516	0·3175	26·82	26·22	−3·00
0·2	8·523	0·3177	26·82	26·22	−3·00
1·0	11·790	0·4201	28·05	25·96	−2·09
1·0	14·970	0·5443	27·51	25·65	−2·02
Strontium nitrate:					
1·0	8·340	0·3172	26·29	26·22	−0·07
1·0	6·739	0·2535	26·59	26·26	−0·31
1·0	5·045	0·1892	26·67	26·30	−0·37
Barium bromide:					
0·297	4·959	0·1894	26·18	26·30	+0·40
0·241	8·287	0·3204	25·86	26·21	1·45
Barium chloride:					
1·0	8·284	0·3293	25·15	26·19	+1·06
0·8	8·305	0·3279	25·33	26·19	1·07
0·4	8·307	0·3263	25·46	26·19	1·82
0·8	3·290	0·1290	25·51	26·33	1·02
0·8	4·882	0·1942	25·14	26·29	1·45
0·8	9·871	0·3971	24·85	26·03	1·47
0·4	13·303	0·5298	25·11	25·73	1·42

water, and we have already shown that this diminution of absorptive power is approximately proportional to the concentration of the dissolved salt. The influence of these salts was found to be greatest for potassium salts, and least for lithium salts, the order of magnitude being potassium, sodium, ammonium, lithium. The experimental data represent the superposed influences of physical action and the formation of chemical complexes, and from the negative values obtained for

$\frac{k - k'}{n}$ with some of the lithium salts we conclude that in these cases the fixation of ammonia in the form of chemical complexes more than counterbalances the lowering of the absorptive power which would result from the purely physical action of the dissolved salt.

The alkaline earth metals approximate in their behaviour to the alkali metals. For the barium salts investigated, the physical action preponderates, whereas in the case of the calcium salt, this physical action is more than counterbalanced by the formation of complex calcium-ammonia ions. These two opposed actions are of approximately equal magnitude for the strontium salt investigated, and in consequence, the value of the distribution coefficient differs but little from that for pure water and chloroform.

The arrangement of the alkaline earth metals in the series barium, strontium, calcium, corresponds with that of the series given above for the alkali metals. The tendency to form complex ammonia ions on the part of calcium is greater than that observed in the case of any of the alkali metals, but it is still very small in comparison with that found for the metals copper, zinc, cadmium, and nickel.

The value of the expression $\frac{k - k'}{n}$ was found to be constant for the alkali salt solutions when both the salt and the ammonia concentrations varied. This constancy is in harmony with the conception that the preponderating action of the dissolved salt is of a physical nature. When the formation of ammonia complexes is very considerable, as with copper, zinc, cadmium, and nickel salts, then this expression is by no means constant. Examination of the previous table shows that $\frac{k - k'}{n}$ is not nearly so constant as in the case of the majority of the alkali salt solutions investigated, and this is probably explainable by the greater tendency towards the formation of ammonia complexes exhibited by the calcium, strontium, and barium salts.

Finally, we may compare our results with those arrived at by Konowaloff (*loc. cit.*) and by Gaus (*loc. cit.*). Konowaloff's results were obtained by determining the partial pressure of normal ammonia solution containing 1 gram-equivalent of salt per litre at 60°, and those of Gaus by determining the same at 25° with solutions which were normal with respect to ammonia and 0·4 normal with respect to salt. The following table contains the values of $P_1 - P$, P_1 being the ammonia pressure over pure water, and P that over the salt solution. For the comparison we make use of an approximate value of $\frac{k - k'}{n}$ which is a measure of the total action.

		$BaCl_2$.	$SrCl_2$.	$Sr(NO_3)_2$.	$CaCl_2$.
		2	2	2	2
Konowaloff.....	$P_1 - P$	+1·05	−1·1	−1·2	−3·6
Gaus	$P_1 - P$	−0·02	−0·29	—	−0·77
Distribution method ...	$\frac{k-k'}{n}$	+1·3	—	−0·3	−2·0

The agreement between the three series is as close as might be expected, the only anomaly being that Gaus finds for barium chloride a negative value, whilst the experiments of Konowaloff and ourselves give a positive value.

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CXII.—*Metal-Ammonia Compounds in Aqueous Solution. Part IV. The Influence of Temperature on the Dissociation of Copper-Ammonia Sulphate.*

By H. M. DAWSON and J. McCRAE.

IT has already been shown (this vol., p. 496) that the distribution of ammonia between water and chloroform at 20° is not quite independent of the concentration, and the variation is exhibited by the distribution coefficient curve on p. 497. In our first communication (Trans., 1900, 77, 1239), we have shown that a complex compound, probably $Cu4NH_3{\cdot}SO_4$, is formed when excess of ammonia is added to a solution of copper sulphate; this complex compound is dissociable, and only when there is a large excess of ammonia in the solution does the number of fixed ammonia molecules per atom of copper approximate to four. We have been able to follow the extent of this dissociation at constant temperature with decreasing total ammonia concentration, and now we have endeavoured to ascertain the influence of temperature on the dissociation.

On account of the method which we employ, it was impossible to use a temperature much above the ordinary, and we have not deemed it advisable to work above 30°, which is our upper limit. For lower temperatures, we are only limited by the freezing point of the solution, but the lowest temperature at which we found it convenient to work was 10°. This gives us a range of 20°, and it was expected that the extent of dissociation at the lower and higher temperatures would be sufficiently different to indicate the temperature influence.

Distribution of Ammonia between Water and Chloroform at varying Temperatures.

The method of experimentation was exactly as has been described in our previous communications (*loc. cit.*). In order to ascertain the amount of ammonia fixed by the salt in solution from the distribution coefficient determined with this solution, it is necessary to know the distribution ratio between pure water and chloroform, and since this varies very considerably with the temperature, determinations of the latter had to be carried out at different temperatures. The temperatures chosen were 10° and 30°, and the following results were obtained :

Concentration of NH_3 in aqueous part. Grams per litre. c_1.	Concentration of NH_3 in the chloroform. Gram per litre. c_2.	Distribution coefficient, $\frac{c_1}{c_2}$ k.
Temperature 10° :		
5·211	0·1686	30·91
6·974	0·2261	30·84
8·123	0·2633	30·84
8·701	0·2847	30·57
12·835	0·4253	30·18
17·370	0·5854	29·67
17·428	0·5862	29·73
Temperature 30° : *		
5·092	0·2250	22·63
6·658	0·2949	22·57
8·497	0·3751	22·65
10·203	0·4558	22·39
11·660	0·5232	22 29
13·601	0·6133	22·18
16·660	0·7575	22·00

* In a previous publication (Trans., 1900, **77**, 1243), we have given the coefficient at 30° as 23·2, but we prefer to take the numbers given above for the reason pointed out on p. 496.

These figures show exactly the same relationships as those previously obtained for the distribution coefficient at 20° (this vol., p. 496), namely, for solutions less than 0·5 normal with respect to ammonia the distribution coefficient remains practically constant at constant temperature, but with more concentrated solutions this ratio diminishes with increasing concentration of the ammonia. The variation of the distribution coefficient within the same limits of ammonia concentration is very nearly the same at the three temperatures, consequently the curve

given on p. 497 may be used to express the results obtained at 10° and 30° if we add to the ordinate 4·54, or subtract from it 3·66. In other words, the three curves representing the dependence of the distribution coefficient on the ammonia concentration at the different temperatures are almost parallel.

It is evident that the distribution coefficient at constant ammonia concentration is not a linear function of the temperature, for the difference in the coefficient for 10° (from 20° to 30°) is in one case 3·66 units, whilst in the other case, for 10° (from 10° to 20°), it is 4·54.

The results obtained have been plotted as curves (not reproduced here), and from these the values at any concentration of ammonia can be read off.

Experiments at 10° *and* 30° *with Copper Sulphate Solutions.*

At 10° and 30°, experiments were made with 0·1 normal copper sulphate solutions, and at 10° with 0·05 normal solutions. The results so obtained are recorded below, and they may be compared with those which we have previously found at 20°.

In the table on p. 1075 we give the various data, the molecules of ammonia fixed per molecule of salt (or per atom of copper) being calculated from the formula $\frac{c_1 - kc_2}{17{\cdot}07} \cdot \frac{2}{n}$, in which k is the distribution coefficient for pure water at the same concentration of ammonia in the chloroform, c_1 and c_2 the observed ammonia concentrations in the aqueous and chloroform layers, and n the normality of the salt solution. We are unable to take account of the physical action of the dissolved material, but, as already stated (p. 511), we believe this to be, in the case of copper salts, very small.

When the distribution coefficient attains a high value, corresponding to a small amount of free ammonia in the salt solution, the error in the determination of the fixed ammonia may be relatively large on account of the small quantity of acid used in the titration of the chloroform. Further, if the coefficient is not much greater than that for pure water, the accuracy is not great, since the calculation involves the difference between these two values. The most accurate values are those obtained when the concentration of ammonia in the aqueous phase is between 6 and 9 grams per litre. As no extreme accuracy can be claimed for the individual figures, we have drawn smoothed curves representing the molecular amount of ammonia fixed per atom of copper in 0·1 N solution at 10°, 20°, and 30° with varying ammonia concentration. The numbers for 20° have been recalculated in accordance with the later determina-

Concentration of NH_3 in aqueous layer. Grams per litre. c_1.	Concentration of NH_3 in $CHCl_3$. Gram per litre. c_2.	Distribution coefficient. K'.	Coefficient corresponding to c_2 for water. k.	Molecular ratio of $CuSO_4$: fixed NH_3. $\frac{c_1 - kc_2}{17{\cdot}07} \cdot \frac{2}{n}$
Temperature 10°.				
0·1 *N* copper sulphate:				
5·427	0·0765	70·92	30·94	1 : 3·52
6·688	0·1153	58·01	30·91	3·66
7·171	0·1317	54·45	30·89	3·64
8·322	0·1679	49·56	30·88	3·68
8·931	0·1872	47·71	30·87	3·69
10·675	0·2446	43·65	30·82	3·67
13·130	0·3273	40·12	30·57	3·66
0·05 *N* copper sulphate:				
3·580	0·0666	53·76	30·94	3·56
5·347	0·1224	43·68	30·90	3·66
7·095	0·1786	39·73	30·87	3·70
9·800	0·2679	36·58	30·75	3·66
Temperature 30°.				
0·1 *N* copper sulphate:				
5·347	0·1072	49·86	22·66	3·42
7·062	0·1790	39·45	22·64	3·53
8·650	0·2441	35·44	22·62	3·66
10·310	0·3170	32·55	22·60	3·68
11·960	0·3915	30·55	22·52	3·68
13·720	0·4699	29·21	22·39	3·76

tions of the distribution coefficient between pure water and chloroform at this temperature. Instead of reproducing these curves, we have constructed the table given on p. 1076 indicating points on the curves.

As would be expected, the figures indicate that, at constant ammonia concentration, the extent of dissociation increases as the temperature rises, and it may be stated that if a comparison be made between the numbers obtained with 0·05 *N* copper sulphate solutions at 10° and 20°, the same conclusion is evident. The differences between the numbers obtained at the different temperatures are, however, too small to admit of any quantitative statement as to the influence of

Table showing the number of molecules of ammonia fixed per atom of copper in 0·1 N solution.

Concentration of NH_3 in the aqueous phase.	10°.	20°.	30°.
6 grams per litre	3·55	3·46	3·42
7 ,, ,, ...	3·63	3·55	3·51
8 ,, ,, ...	3·67	3·61	3·58
9 ,, ,, ...	3·70	3·67	3·62

temperature on the dissociation of the complex copper ammonia sulphate.

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CXIII.—*Additional Notes on Dinitro-o-anisidine. A Chemical Reaction in which one of the Products continues the same Reaction.*

By RAPHAEL MELDOLA, F.R.S., and JOHN VARGAS EYRE.

THE dinitroanisidine described last year by one of the authors and Elkan Wechsler (Trans., 1900, 77, 1172) has been since shown to have the constitution 4 : 5-dinitro-2-aminoanisole (Proc., 1901, 17, 131; also Freyss, *Bull. Soc. Ind. Mulhouse*, 1901, 70, 375). Further evidence of this constitution is given in the following paper as well as some experiments which throw light on the remarkable action of nitrous acid on the compound.

The Diphenylazines from the Triaminoanisole and its Acetyl Derivatives.

Dinitroacetanisidide (m. p. 162—163°) was reduced in glacial acetic acid solution with zinc dust and a few drops of hydrochloric acid to start the reaction. The solution containing the acetyltriaminoanisole was mixed with an acetic acid solution containing the calculated quantity of benzil, and the mixed solutions heated for some hours on a water-bath. The azine is thrown out on dilution with water, and neutralisation with ammonia as an ochreous powder which dissolves in boiling alcohol with a brownish colour. The solution is slightly fluorescent

when cold, and the azine separates in the form of ochreous needles melting at 223—224°.

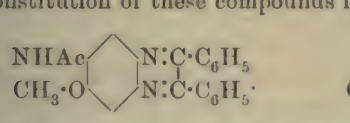
0·1163 gave 11·8 c.c. moist nitrogen at 20·5° and 764 mm. N = 11·62.
0·1186 „ 11·75 „ „ 19·5° „ 752·4 mm. N = 11·23.
$C_{23}H_{19}O_2N_3$ requires N = 11·39 per cent.

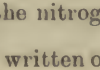
The dinitroanisidine on similar treatment gave an azine crystallising from alcohol in brown needles with serrated edges, and from benzene, in which it is very soluble, in minute, pale, ochreous needles. The melting point is 194—195°.

0·1092 gave 12·2 c.c. moist nitrogen at 18·5° and 755·8 mm. N = 12·78.
0·0903 „ 10 „ „ 20·5° „ 770·5 mm. N = 12·80.
$C_{21}H_{17}ON_3$ requires N = 12·84 per cent.

The dilute alcoholic solution of the azine has a distinct green fluorescence which disappears on heating, and reappears on cooling. The compound is basic and dissolves in strong hydrochloric acid with a claret red colour, which disappears on dilution with water, owing to the dissociation of the salt.

The constitution of these compounds is shown by the formulæ:

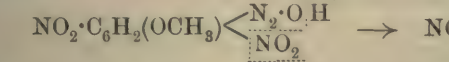


The azine ring may of course be represented in the usual way with a cross linking between the nitrogen atoms:  , or the left-hand benzene ring may be written on the quadrivalent (quinonoid) type:



Quantitative Diazotisation of Dinitro-o-anisidine.

It has been proved in former papers that this compound loses a nitro-group on diazotisation, and we have shown in our last note (Proc., 1901, **17**, 131) that the nitro-group thus eliminated is the one occupying the para-position with respect to the amino-group, the resulting compound being a diazoxide. In the note referred to, we suggested that the nitro-group might be eliminated in the form of nitrous acid according to the scheme:



If this view were correct, we should have the somewhat remarkable case of a chemical reaction in which one of the products (nitrous acid)

is the same as the reagent added, and is thus capable of carrying on the diazotisation. In order to submit this to the test of experiment, a method had to be devised for measuring quantitatively the amount of diazotising work done by a known quantity of nitrous acid. Preliminary experiments with a standardised solution of sodium nitrite, and solutions of known strength of dinitroanisidine in glacial acetic acid, showed that the ordinary method of ascertaining the end of diazotisation by the liberation of free nitrous acid was quite inapplicable in the present case. Free nitrous acid, as shown by the potassium iodide and starch test, shows itself from the very first addition of the nitrite solution, and does not cease to be present until after some days. In other words, the diazotising process has no time limit sharp enough to be fixed by any colour test. Under these circumstances, we were led to use the gravimetric method formerly applied with success in the case of the quantitative resolution of the diazoamido-compounds (Meldola and Streatfeild, Trans., 1887, **51**, 438; 1888, **53**, 675). The method as applied to the present reaction depends upon the following conditions:

If sodium nitrite solution is added to an acetic acid solution of dinitroanisidine, keeping the latter in excess, there are present after a certain interval (1) diazoxide, (2) unaltered dinitroanisidine, and (3) nitrous acid. After a sufficiently long interval (about 3 days), free nitrous acid is no longer detectable, but even if free nitrous acid is present this does not interfere with the results. On adding such a solution to an alkaline solution of β-naphthol, the diazoxide combines at once to form the azo-compound, $NO_2 \cdot C_6H_2(OCH_3)(OH) \cdot N_2 \cdot C_{10}H_6 \cdot OH$.* On making strongly acid with hydrochloric acid, the free azo-compound is precipitated, whilst the unaltered dinitroanisidine remains in solution if a sufficient volume of water is present. The azo-compound, being practically insoluble in water (even when hot), can be collected on a tared filter, washed with dilute acid, and finally with hot water, until free from all soluble compounds, and then dried and weighed. The weight of azo-compound gives the weight of diazoxide formed.

Two sets of experiments were made, using the following quantities:

A.—*First Set.*—Twenty-five c.c. of a 1 per cent. solution of dinitroanisidine in acetic acid. Sodium nitrite solution 1 c.c. = 0·0029 gram $NaNO_2$.

B.—*Second Set.*—Same quantities of dinitroanisidine. Nitrite solution 1 c.c. = 0·00906 gram $NaNO_2$.

* The formula of this compound given in the preliminary note (Trans., 1900, **77**, 1173) does not represent it as containing a hydroxy- as well as a methoxy-group, because the nature of the reaction had not been at that time fully made out. The percentage of nitrogen does not differ considerably in the two cases.

The quantity of dinitroanisidine was the same throughout, 0·25 gram, and the same quantity of nitrite, 0·0202 gram, was added in each case, namely, 6·98 c.c. in set A, and 2·23 c.c. in set B. This quantity of nitrite is *one-fourth* the calculated quantity required on the assumption that one molecule of dinitroanisidine requires one molecule of nitrite. The results are given below:

		Dinitro-anisidine.	Time.	Nitrite.	Weight of β-naphthol.	Weight of azo-compound.
A	I ...	0·25	4 days	0·0202	0·2	0·3498
	II ...	,,	5 ,,	,,	,,	0·3806
B	III ...	,,	3 ,,	,,	,,	0·2867
	IV ...	,,	4 ,,	,,	,,	0·3198
	V ...	,,	5 ,,	,,	,,	0·3694

The β-naphthol is slightly in excess of that required by theory, namely, 0·2 instead of 0·17 gram, but this excess is completely removed during the treatment. The quantity of azo-compound theoretically producible by the weight of nitrite taken (0·0202 gram) is 0·0992 gram. The weight of azo-compound theoretically producible on the assumption that all the dinitroanisidine is converted into diazoxide is 0·3968 gram. Thus the results show that whilst the theoretical limit of diazotisation is not reached in five days, the actual amount of diazoxide formed is greatly in excess of that capable of being produced by the weight of nitrite added. *The nitro-group eliminated thus continues the diazotisation.*

The method, although not claiming to give results within very close limits of accuracy, is sufficiently exact to bring out this main conclusion in a very striking manner. The only sources of error that can be foreseen are the solubility of the azo-compound in water leading to a deficiency and the possible retention of dinitroanisidine leading to an excess in weight. The first of these errors we believe to be quite negligible. The second was provided against by washing the azo-compound (after being collected) off the filter, redissolving in hot dilute sodium hydroxide, reprecipitating by acid, and collecting and washing again before drying and weighing. The azo-compound in each experiment was thus twice precipitated from a large volume of dilute acid, and although a slight loss may have been incurred by this treatment, the final product was pure azo-compound as shown by analysis.

0·1174 of No. II gave 12·85 c.c. moist nitrogen at 21° and 757·4 mm. N = 12·40.

$C_{17}H_{13}O_5N_3$ requires N = 12·39 per cent.

FINSBURY TECHNICAL COLLEGE.

CXIV.—*Some relations between Physical Constants and Constitution in Benzenoid Amines. Part II.*

By Paul Gordan and Leonhard Limpach.

This paper is a continuation of the discussion of the relationship between "Melting Points and Constitution in some Amines" on which a preliminary note was published in 1893 by W. R. E. Hodgkinson and L. Limpach (Proc., 9, 41).

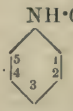
By replacing the benzenic hydrogen in formoanilide and acetanilide by methyl, 38 compounds can be obtained. If the number of introduced methyl groups be ρ, then the values 0 : 1 : 2 : 3 : 4 : 5 * represent the number, ρ, of the anilide, toluidides, xylidides, and amino-trimethyl, -tetramethyl, and -pentamethyl derivatives respectively.

This series, R, comprises 1 : 3 : 6 : 6 : 3 : 1 compounds. The melting points of 36 of these 40 compounds have been actually determined, and are given in Table 1.

Table 1.

Formyl compounds.		Acetyl compounds.	
Formanilide [0]	46°	Acetanilide [0]	114°
Formotoluidides.		**Acetotoluidides.**	
1	58°	1	107°
2	liquid	2	65·5
3	52°	3	147
Formoxylidides.		**Acetoxylidides.**	
1 : 2	103·5°	1 : 2	134°
2 : 3	68	2 : 3	99
1 : 5	164	1 : 5	177
1 : 3	113·5	1 : 3	129
2 : 4	76·5	2 : 4	142·5
1 : 4	116·5	1 : 4	138·5

* As a matter of convenience, the positions in formanilide are numbered thus :



so that positions 1 and 5 are relatively ortho to the formyl or acetyl groups respectively.

TABLE 1 (*continued*).

Formyl compounds.		Acetyl compounds.	
Formanilide [0]	46°	Acetanilide [0]	114°
Formylaminotrimethylbenzenes.		**Acetylaminotrimethylbenzenes.**	
1 : 3 : 5	176°	1 : 3 : 5	216·5°
2 : 3 : 5	120·5	2 : 3 : 5	164
1 : 2 : 4	98	1 : 2 : 4	126
1 : 4 : 5		1 : 4 : 5	
1 : 2 : 3		1 : 2 : 3	
2 : 3 : 4	98·5	2 : 3 : 4	164·5
Formylaminotetramethylbenzenes.		**Acetylaminotetramethylbenzenes.**	
1 : 2 : 3 : 4	143·5°	1 : 2 : 3 : 4	169°
1 : 2 : 3 : 5	183	1 : 2 : 3 : 5	215·5
1 : 2 : 4 : 5	164	1 : 2 : 4 : 5	192
Formylaminopentamethylbenzene.		**Acetylaminopentamethylbenzene.**	
1 : 2 : 3 : 4 : 5	216·5°	1 : 2 : 3 : 4 : 5	215·5°

The first step in the investigation was to obtain such an arrangement of these 36 melting point values that certain regularities should appear.

Averages D_1 and D_2 were found for the series R.

The values D_1 of series R are obtained by adding all the melting point values of the compounds and dividing by the number of compounds. The values D_2 by adding the highest and lowest melting points and dividing by 2. It will be observed from Table 2, firstly,

TABLE 2.

Compounds.	N_1.	N_2.	D_1.	D_2.
Formanilide	54·4	47·6	46	46
Formotoluidides	81·6	81·6		
Formoxylidides	108·8	115·6	107	116
Formylaminotrimethylbenzenes	136	149·6		
Formylaminotetramethylbenzenes	163·2	183·6	163·7	163·2
Formylaminopentamethylbenzenes	190·4	217·6	216·5	216·5
Acetanilide	81·6	115·6	114	114
Acetotoluidides	108·8	136	106·5	106·2
Acetoxylidides	136	156·5	136·7	138
Acetylaminotrimethylbenzenes	163·2	176·8		171·2
Acetylaminotetramethylbenzenes	190·4	197·2	192	192·2
Acetylaminopentamethylbenzenes	217·6	217·6	215·5	215·5

that the differences between D_1 and D_2 are small, and secondly, that they differ but little from certain values, N_1 and N_2, which are given and defined by the formulæ:

$$N_1 = \begin{cases} 4.6'8(\rho+2) \text{ for formyl compounds.} \\ 4.6'8(\rho+3) \text{ for acetyl } \text{,,} \end{cases}$$

$$N_2 = \begin{cases} 6'8(5\rho+7) \text{ for formyl compounds.} \\ 6'8(3\rho+7) \text{ for acetyl } \text{,,} \end{cases}$$

The values of N_1, N_2, D_1, D_2, are shown in Table 2, and the differences $N_2 - N_1$, $D_1 - N_1$, $D_1 - N_2$, $D_2 - D_1$, in Table 3.

TABLE 3.

Compounds.	$N_2 - N_1$.	$D_1 - N_1$.	$D_1 - N_2$.	$D_2 - D_1$.
Formanilide	−6·8	−8·4	−1·6	0
Formotoluidides	0			
Formoxylidides	6·8	−1·8	−7·9	0
Formylaminotrimethylbenzenes	13·6			
Formylaminotetramethylbenzenes	20·4	0·5	−19·9	−0·5
Formylaminopentamethylbenzenes	27·2	26·1	−1·1	0
Acetanilide	34	32·4	−1·6	0
Acetotoluidides	27·2	−2·3	−29·5	−0·3
Acetoxylidides	20·4	0·7	−19·7	1·3
Acetylaminotrimethylbenzenes	13·6			
Acetylaminotetramethylbenzenes	6·8	1·6	−4·8	0·2
Acetylaminopentamethylbenzenes	0	−2·1	−2·1	0

The melting points of the 36 compounds can be arranged in three primary classes (Table 4), and the third class again can be divided into 2 sub-classes.

The first class contains 6 formyl and 9 acetyl derivatives, the melting points of which fall between the values N_1 and N_2, or differ, at most, about 2° from them.

The second class comprises 2 formyl and 4 acetyl compounds, the melting points of which are more than 2° higher than the values in N_1 and N_2.

The first of these compounds is *p*-acetotoluidide and all the others contain methyl groups substituted in the 1 : 5 positions.

In the third class are 10 formyl and 5 acetyl compounds: their melting points are more than 2° lower than indicated under N_1 and N_2. Of these 15 compounds, 9 belong to the second sub-class, they contain methyl groups substituted in the 2 : 3 or 2 : 4 positions.

The melting points of formyl derivatives differ more amongst themselves than do the melting points of acetyl derivatives.

Four compounds have very high melting points not differing more than 1° from 216°.

TABLE 4.

1st Class.

Formyl derivatives.

[0] = 46°; [1 : 3] = 113·5°; [1 : 4] = 116·5°; [1 : 2 : 3 : 5] = 183°; [1 : 2 : 4 : 5] = 164°; [1 : 2 : 3 : 4 : 5] = 216·5°.

Acetyl derivatives.

[0] = 114°; [1] = 107°; [1 : 2] = 134°; [1 : 4] = 138·5°; [2 : 4] = 142·5°; [2 : 3 : 5] = 164°; [2 : 3 : 4] = 164·5°; [1 : 2 : 4 : 5] = 192° [1 : 2 : 3 : 4 : 5] = 215·5°.

2nd Class.

Formyl derivatives.

[1 : 5] = 164°; [1 ; 3 : 5] = 176°.

Acetyl derivatives.

[3] = 147°; [1 : 5] = 177°; [1 : 3 : 5] = 216·5°; [1 : 2 : 3 : 5] = 215·5°

3rd Class.

1st Sub-class.

Formyl derivatives.

[1] = 58°; [2] = fluid; [3] = 52°; [1 : 2] = 103·5°.

Acetyl derivatives.

[2] = 65·5°; [1 :3] = 129°.

2nd Sub-class.

Formyl derivatives.

[2 : 3] = 68°; [2 : 4] = 76·5°; [1 : 2 : 4] = 98°; [2 : 3 : 4] = 98·5°; [2 : 3 : 5] = 120·5°; [1 : 2 : 3 : 4] = 143·5°.

Acetyl derivatives.

[2 : 3] = 99°; [1 : 2 : 4] = 126°; [1 : 2 : 3 : 4] = 169°.

As previously mentioned, 36 only of the 40 possible compounds of this class have had their melting points determined. Both the formyl- and acetyl-amino-1 : 4 : 5- and 1 : 2 : 3-trimethylbenzenes are missing.

The melting points of these substances can be approximately calculated. The differences, $D_1 - N_1$, given in Table 3 are but small (with the exceptions of aniline and aminopentamethylbenzene, which give small differences $D_1 - N_2$).

It may, therefore, be pretty safely assumed that for the two missing substances these numbers would also be small. On this assumption, we may take the average of D_1 as 136° for formylaminotrimethylbenzenes, and 170° for the corresponding acetyl compounds. For the formylaminotrimethylbenzenes, the average of D_2 may be taken as 5° higher than D_1, so that D_2 may be about 141°.

In Table 1, the lowest melting point of formylaminotrimethylbenzene is 98°. The 1 : 4 : 5-modification contains the 1 : 5-arrangement, and has, probably, the highest melting point; we have

$$\frac{[1:4:5]+98^\circ}{2} = D_2 = 141^\circ \quad \text{and} \quad [1:4:5] = 184^\circ.$$

The mean value of D_1 for the formylaminotrimethylbenzenes is 136°, we have therefore:

$$[1:3:5] + [2:3:5] + [1:2:4] + [1:4:5] + [1:2:3] + [2:3:4] = D_1 = 136^\circ.$$

Introducing the values from Table 1,

$$\frac{176^\circ + 120{\cdot}5^\circ + 98^\circ + 184^\circ + [1:2:3] + 98{\cdot}5^\circ}{6} = 136^\circ,$$

from which we calculate for the 1 : 2 : 3-derivative the melting point 135°.

With the acetyl derivatives, the case is somewhat different: the one of constitution [1 : 3 : 5] has the highest melting point of all, 216·5°, and the 1 : 2 : 4-derivative the lowest, namely, 126°.

D_2 does not affect the melting points of the 1 : 4 : 5- and the 1 : 2 : 3-derivatives. Of these melting points, that of the 1 : 4 : 5-compound is no doubt the higher, and the difference between them may be about 30°. [1 : 4 : 5] − [1 : 2 : 3] = 30°.

By the formula

$$\frac{[1:3:5] + [2:3:5] + [1:2:4] + [1:4:5] + [1:2:3] + [2:3:4]}{6} = D_1 = 170^\circ.$$

Introducing the values from Table 1,

$$\frac{216{\cdot}5^\circ + 164^\circ + 126^\circ + [1:4:5] + [1:2:3] + 164{\cdot}5^\circ}{6} = 170^\circ.$$

therefore $[1:4:5] + [1:2:3] = 350^\circ$ $\begin{matrix}[1:4:5] = 190^\circ. \\ [1:2:3] = 160^\circ.\end{matrix}$

It will be seen from Table 1 that the melting points of the acetyl derivatives are higher than those of the corresponding formyl compounds. This is more clearly shown in Table 5.

TABLE 5.

Bases.	Constitution.	Formyl compound.	Acetyl compound.	Difference.
Aniline	—	46°	113—114°	67°
Toluidine	1	58	107	49
,,	2	liquid	65·5	
,,	3	52	147	95
Xylidine	1 : 2	103·5	134	30·5
,,	2 : 3	68	99	31
,,	1 : 5	164	177	13
,,	1 : 3	113·5	129	13·5
,,	2 : 4	76·5	142·5	66
,,	1 : 4	116·5	138·5	22
Aminotrimethylbenzene	1 : 3 : 5	176	216·5	40·5
,, ,,	2 : 3 : 5	120·5	164	43·5
,, ,,	1 : 2 : 4	98	126	28
,, ,,	1 : 4 : 5	184	190	6
,, ,,	1 : 2 : 3	135	160	25
,, ,,	2 : 3 : 4	98·5	164·5	66
Aminotetramethylbenzene	1 : 2 : 3 : 4	143·5	169	25·5
,, ,,	1 : 2 : 3 : 5	183	215·5	32·5
,, ,,	1 : 2 : 4 : 5	164	192	28
Aminopentamethylbenzene	1 : 2 : 3 : 4 : 5	216·5	215·5	−1

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CXV.—*The combined Action of Diastase and Yeast on Starch-granules.*

By GEORGE HARRIS MORRIS, Ph.D., B.Sc.

IT has long been known that when starch conversions, containing high type malto-dextrins or the so-called stable dextrin, are acted on by yeast in the presence of diastase, the action is very greatly in excess of that produced by either yeast or diastase acting separately; in fact, the so-called stable dextrin, which is not acted on either by yeast or by diastase under ordinary conditions, may be completely fermented by yeast in the presence of active diastase.

Some experiments described a few years ago by J. Vuylsteke (*Bull. Acad. roy. Belgique*, 1892, [iii], 24, 577), in which he showed that certain starches, in the solid state, might be fermented by yeast in the presence of malt extract, led me to examine the question whether, in

this case also, the combined action of yeast and diastase exceeded that of either when acting alone.

To this end, 100 grams of barley-starch were digested with 50 c.c. of normal cold water malt extract and 250 c.c. of water, with constant agitation in a Dunstan's laboratory shaking machine. Side by side with this, the same quantities of starch, malt-extract, and water were digested with the addition of 10 grams of washed and pressed yeast, the gas evolved being passed through a small wash-bottle. At the end of 72 hours the two experiments were stopped, in the first the residual starch was filtered off, and the specific gravity, the optical rotation, and the cupric reducing power of the filtrate determined in the usual way; in the second, the residual starch and yeast were also removed by filtration, the alcohol in the filtrate determined by distillation, and the specific gravity, the optical rotation, and the cupric reducing power determined in the residue after making up to the original volume.

The results obtained were*:

(a) *Barley-starch with malt-extract alone.*

Specific gravity	1021·6.
Optical activity in 100 mm. tube	20·7 divisions.
Cupric reducing power on 100 c.c.	6·198 grams CuO.

(b) *Barley-starch with malt-extract and yeast.*

Alcohol per 100 c.c.	7·95 grams.
Specific gravity of residue	1007·27.
Optical activity in 100 mm. tube	2·4 divisions.
Cupric reducing power on 100 c.c.	0·8624 gram CuO.

Control experiments were made in each case with malt-extract alone, and the above numbers are corrected for the results so obtained.

When the excess specific gravity of the filtrate in (a) is divided by 3·934, the divisor for maltose at this density, it is found that the solid matter in solution per 100 c.c. is 5·490 grams; calculated from the optical activity, the quantity per 100 c.c. is 5·201 grams, and from the cupric reducing power, 4·608 grams per 100 c.c. These numbers are sufficiently close to allow of the conclusion that the substance in solution is maltose, and on the basis of the specific gravity, we find that 16·470 grams have gone into solution in the 92 hours. This corresponds to the dissolution of 15·6 per cent. of the starch employed.

In the second experiment (b) in which diastase (malt-extract) and

* For a description of the methods used, see "Experimental methods employed in the examination of the products of Starch-hydrolysis by Diastase" (Brown, Morris, and Millar, Trans., 1897, **71**, 72—108).

yeast were allowed to act conjointly, the amount of alcohol formed by the fermentation corresponds to 15·437 grams of maltose fermented per 100 c.c., and the cupric reducing power of the residue to a further 0·624 gram of maltose per 100 c.c.; the optical activity required by this amount of maltose is 2·48 divisions, against 2·4 observed. The specific gravity of the residue indicates the presence of 1·85 grams of solid matter per 100 c.c., but as this includes the non-volatile products of fermentation it does not correctly represent the soluble products directly derived from the starch. The soluble products in this case may therefore be taken as $15{\cdot}437 + 0{\cdot}624 = 16{\cdot}061$ grams per 100 c.c., or 48·183 grams in all. This means that 45·6 per cent. of the starch had been decomposed.

There was therefore a greatly increased action of the diastase in the presence of yeast, the quantity of starch which went into solution being nearly three times the amount dissolved by the diastase alone.

It appeared possible that this increased action might be due to the removal by fermentation of the soluble starch-products first formed by the action of the diastase on the starch-granules, thus allowing the enzyme to act more freely on the remaining granules. Opposed to this, however, was the consideration that the alcohol formed during fermentation would probably exercise as great a retarding influence on the diastase as would the soluble starch-products.

In order to examine this possibility, 10 grams of barley-starch were shaken with 25 c.c. of cold water malt-extract and 100 c.c. of water, side by side with similar quantities of starch and malt-extract, but with the addition of 100 c.c. of a solution of starch-products in place of the water. After 24 hours, both mixtures were filtered and examined as described above. It was found that there was only a difference of 0·24 gram per 100 c.c. in the quantity of starch dissolved in the two experiments. This point was further tested by taking 20 grams of barley-starch, mixing it with 50 c.c. of cold water malt-extract and 200 c.c. of water, and solidifying the whole with 3 per cent. of gelatin. The mixture was divided into two portions, one being allowed to stand for 24 hours, and the other placed in a dialysing tube, surrounded with distilled water, for 24 hours. At the end of that time, the two experiments were examined as before, and it was found that the amount of substance dissolved in the first experiment was exactly the same as the sum of the soluble products remaining in the dialysing tube *plus* the maltose which had diffused into the water surrounding it. In the first, the density of the solution, after making all due corrections, was 1010·0, in the second, 1010·1 (water = 1000).

It then appeared desirable to ascertain (*a*) whether the presence of yeast, under conditions which prevented the exercise of its fermentative power, had an effect similar to that which it exerted when

able to ferment the soluble products formed by the diastase, and (*b*) whether any increased activity was conferred on the diastase of the malt-extract by the vital activity of the yeast during fermentation.

With this end in view, a series of three experiments was made. In (1) 10 grams of barley-starch were digested with 25 c.c. of malt-extract, 100 c.c. of water, and 2 grams of washed and pressed yeast for 24 hours; in (2) the same quantities of starch, malt-extract, yeast, and water were digested in the shaking machine for 24 hours in the presence of a small quantity of chloroform, in order to check the fermentative activity of the yeast; and in (3) 25 c.c. of malt-extract were mixed with 100 c.c. of water and 2 grams of yeast and allowed to stand until the fermentation was complete. The liquid was then filtered, and the clear filtrate digested with 10 grams of starch in the shaking machine for 24 hours.

After each experiment had proceeded for 24 hours, the residual starch was filtered off, and the filtrates examined as described above. In (1) and (3) the "original gravities" * were determined and compared with the specific gravity of the solution in (2). The results were as follows:

(1) "Original gravity"	1010·34
(2) Specific gravity	1005·29
(3) "Original gravity"	1006·50

These experiments show that neither the presence of non-fermentative yeast-cells nor the influence of fermentation on the diastase of the malt-extract had the effect of bringing about the dissolution of the same amount of starch as had the combined action of malt-extract and active yeast.

In all these experiments, the matter in solution, or remaining in solution unfermented, had an optical activity and cupric reducing power corresponding to the presence of maltose only.

A furthur experiment was made to determine whether agitation alone had any influence on the action of diastase on starch-conversion products. For this purpose, a solution of transformation products of high rotatory power was made by converting a starch paste with malt-extract in the usual way. After boiling and filtering the solution, it was divided into two portions, to each of which 5 c.c. of cold water malt-extract per 100 c.c. were added. One portion was shaken for 24 hours, the second was allowed to stand without agitation for the same period. The solutions were then analysed, and found to be identical

* It is more convenient to express the matter dissolved in this way, since the alcohol, &c., produced by the fermentation of the malt-extract itself can be more easily corrected for

in composition. Agitation, therefore, is without any influence on the action of diastase.

Finally, the action of precipitated diastase was compared with that of malt-extract.

The experiments were carried out precisely as those first described, with the exception that 50 c.c. of a solution of diastase (containing 0·1 gram of precipitated diastase) were used in place of cold water malt-extract. In the experiment with diastase alone, the quantity of matter which went into solution in 24 hours was comparatively small, amounting only to 0·402 gram per 100 c.c., but when the diastase and yeast acted together, the quantity dissolved was 2·37 grams per 100 c.c., and of this 1·59 grams were fermented. There is therefore a still more marked difference between the action of precipitated diastase alone and that of diastase *plus* yeast, than in the corresponding experiments where cold water malt-extract was employed, although in neither instance is the action so considerable or so rapid.

The analysis of the matter which went into solution under the action of diastase and of that which remained unfermented points to it being a mixture of maltose and dextrin, and not maltose only, as is the case when malt-extract is employed.

Only those starches, the granules of which are attacked by diastase in the cold, undergo fermentation in the presence of diastase and active yeast; thus potato starch, the granules of which are not attacked or dissolved by malt-extract alone, remains absolutely untouched by malt-extract and yeast when acting together.

The foregoing results are especially interesting in view of the attention which has of late been given to instances of so-called symbiotic action between moulds and yeasts, the chief action of the former being apparently to secrete diastase and degrade the starch or starch-products to fermentable sugars which can then be attacked by the yeast. It would appear, however, that there exists an action closely analogous to symbiosis between an unorganised and an organised ferment, and it may be doubted whether the fermentations in which moulds and yeasts are concerned are really instances of true symbiosis, since the former can be replaced by an enzyme with the production of the same result.

CXVI.—*Action of Bromine on the Three Tolueneazophenols.*

By J. T. Hewitt and John N. Tervet.

The action of substituting agents on oxyazo-compounds has been studied somewhat extensively by one of the authors of this communication and his co-workers. It has been generally found that towards dilute nitric acid and bromine (in presence of sodium acetate) these substances behave as true hydroxyl derivatives of azo-substances and not as the tautomeric quinonehydrazones. Whilst, however, the behaviour towards warm dilute nitric acid has been examined, not only in the case of benzeneazophenol itself (Trans., 1900, **77**, 229), but also for three tolueneazophenols (Trans., 1901, **79**, 155) and benzeneazosalicylic acid (Trans., 1901, **79**, 49), no other *p*-hydroxyazo-compound has been studied with regard to its action on bromine.* It seemed, therefore, of some interest to examine other *p*-hydroxyazo-compounds, and for this purpose, the three tolueneazophenols were chosen, since their nitration had already been studied with the result that *m*-tolueneazophenol had been found to nitrate far less smoothly than its two isomerides, and, moreover, when *m*-tolueneazo-*o*-nitrophenol had been obtained, no means were devised of obtaining its acetyl and benzoyl derivatives, although ethyl might easily be introduced in place of hydrogen. We found, however, that *m*-tolueneazodibromophenol not only furnished an ethyl ether but also was acetylated and benzoylated quite normally.

o-*Tolueneazodibromophenol.*

Ten grams of *o*-tolueneazophenol and 20 grams of fused sodium acetate were made into a paste with glacial acetic acid. The mixture was cooled to 10° and 16 grams of bromine, diluted with 40 grams of glacial acetic acid, were slowly added. The dibromo-derivative separated in a crystalline condition, and after a further recrystallisation from boiling glacial acetic acid, it formed yellow needles melting at 121° (corr.).

0·1530 gave 0·2351 CO_2 and 0·0391 H_2O. C = 41·90; H = 2·84.
$C_{13}H_{10}ON_2Br_2$ requires C = 42·16; H = 2·72 per cent.

The substance is very soluble in acetone; fairly so in aniline, benzene, nitrobenzene, ethyl acetate, or ethyl ether; sparingly so in carbon disulphide and chloroform, and nearly insoluble in light petroleum.

* Benzeneazo-*p*-cresol (Hewitt and Phillips, Trans., 1901, **79**, 160) belongs of course to the ortho-series.

The two bromine atoms enter the phenol nucleus, since on reduction with tin and hydrochloric acid, *o*-toluidine is obtained. The presence of the latter was rendered certain by making the reduction product alkaline, blowing steam through the liquid, and shaking the distillate with sodium hydroxide and benzoyl chloride. The benzoyl derivative which separated melted at 139° (uncorr.) after recrystallisation from benzene.

Ethyl Ether.—A solution of 0·2 gram of sodium in 10 c.c. of absolute alcohol was heated with 3 grams of the dibromoazophenol and 1·2 grams of ethyl bromide for 4 hours at 140°. The product was isolated in the usual manner and recrystallised from spirit; it melted at 95°.

0·0719 gave 0·0681 AgBr. Br = 40·30.

$C_{15}H_{14}ON_2Br_2$ requires Br = 40·15 per cent.

The substance, which forms orange plates, is very soluble in benzene, carbon disulphide, ether, or ethyl acetate; fairly so in chloroform or light petroleum, and sparingly so in cold alcohol or acetic acid.

Acetyl Derivative.—Prepared by heating with an equal weight of fused sodium acetate and five times the weight of acetic anhydride. Acetylation is complete after one hour at 100°. When recrystallised from glacial acetic acid, the substance forms orange needles melting at 153°.

0·0992 gave 0·0896 AgBr. Br = 38·43.

$C_{15}H_{12}O_2N_2Br_2$ requires Br = 38·79 per cent.

It is very soluble in carbon disulphide or chloroform, fairly so in aniline, nitrobenzene, acetone, ethyl acetate, or ether, sparingly so in benzene, and nearly insoluble in light petroleum, cold alcohol, or cold acetic acid.

Benzoyl Derivative.—Obtained by boiling with three times its weight of benzoyl chloride for 2½ hours in a reflux apparatus. By pouring into excess of cold spirit, the substance is obtained crystalline, and when once recrystallised from boiling spirit, in which it is very sparingly soluble, small, orange prisms, melting at 168·5°, are obtained. It is fairly soluble in benzene, aniline, nitrobenzene, carbon disulphide, or chloroform.

0·1754 gave 0·1399 AgBr. Br = 33·94.

$C_{20}H_{14}O_2N_2Br_2$ requires Br = 33·73 per cent.

m-*Toluneazodibromophenol.*

In the preparation of this substance, considerable care is necessary. If *m*-toluneazophenol is merely ground up with fused sodium acetate and acetic acid and then brominated, the mixture becomes warm, considerable destruction of the azo-compound takes place, and bromine

derivatives of phenol are formed in considerable quantity. The desired dibromo-derivative may, however, be obtained in nearly quantitative yield, by dissolving 5 grams of *m*-toluenеazophenol in 150 c.c. of glacial acetic acid to which 10 grams of fused sodium acetate have been added. The solution is then carefully cooled to 0° and 8 grams of bromine diluted with 25 grams of glacial acetic acid added drop by drop, the mixture being vigorously stirred, since the bromination product crystallises out nearly completely during the process. Collected and recrystallised from glacial acetic acid, the product is obtained in yellow needles melting at 129°.

0·1417 gave 0·1442 AgBr. Br = 43·00.

$C_{13}H_{10}ON_2Br_2$ requires Br = 43·19 per cent.

The solubilities resemble those of the ortho-compound, but are somewhat greater. The constitution of the substance was determined by reduction; the product, after being rendered alkaline, was distilled with steam, and the *m*-toluidine in the distillate detected by benzoylation. The benzoyl derivative was free from halogen and melted at 119° (121—122° corr.).

The *ethyl ether*, prepared in the usual manner and recrystallised from spirit, forms yellow leaflets melting at 88°. The solubilities of the substance resemble those of the ortho-isomeride.

The *acetyl* derivative, when recrystallised from glacial acetic acid, forms orange needles of considerable brilliancy and melts at 118°.

0·1650 gave 10·3 c.c. moist nitrogen at 23° and 760 mm. N = 7·04.

$C_{15}H_{12}O_2N_2Br_2$ requires N = 6·81 per cent.

It is very soluble in ethyl acetate, benzene, carbon disulphide, or chloroform; fairly so in ether, and nearly insoluble in cold acetic acid.

The *benzoyl* derivative separates from hot spirit, in which it is very sparingly soluble, as very small, pale yellow needles melting at 141°.

0·1865 gave 10·1 c.c. moist nitrogen at 22° and 752 mm. N = 6·17.

$C_{20}H_{14}O_2N_2Br_2$ requires N = 5·90 per cent.

The solubilities of the substance generally resemble those of the isomeric ortho-compound.

p-*Tolueneazodibromophenol.*

This substance was prepared in exactly the same manner as the corresponding derivative of *o*-toluenеazophenol. When recrystallised from glacial acetic acid, it forms dark yellow, shining needles melting at 137°.

0·1744 gave 11·7 c.c. moist nitrogen at 16° and 748 mm. N = 7·67.
$C_{13}H_{10}O_2N_2Br_2$ requires N = 7·58 per cent.

The solubility of the substance in the usual organic solvents is somewhat greater than that of the corresponding *o*-tolueneazodibromophenol. Complete reduction of the compound gave *p*-toluidine as one of the products. After the reduction mixture had been rendered alkaline, steam carried over a volatile base which had a melting point of 45°, and gave the usual tests for *p*-toluidine.

The *ethyl ether* separates from spirit in shining, brownish-yellow needles melting at 95°.

0·0984 gave 0·0927 AgBr. Br = 40·09.
$C_{15}H_{14}ON_2Br_2$ requires N = 40·15.

The substance dissolves readily or fairly easily in most organic solvents, but like its isomerides is sparingly soluble in cold alcohol or acetic acid.

The *acetyl* derivative crystallises from acetic acid in orange needles melting at 148°.

0·1020 gave 0·0942 AgBr. Br = 39·31.
$C_{15}H_{12}O_2N_2Br_2$ requires Br = 38·79.

The solubilities of the substance resemble those of the ortho-compound.

The *benzoyl* derivative separates from boiling spirit, in which it dissolves only sparingly, as orange-yellow prisms melting at 114°.

0·0996 gave 0·0790 AgBr. Br = 33·75.
$C_{20}H_{14}O_2N_2Br_2$ requires Br = 33·73.

Again, the solubilities were found to agree closely with those of the isomeric ortho-compound.

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CXVII.—*Nitrilosulphates.*

By Edward Divers and Tamemasa Haga.

Nitrilosulphates were discovered in 1845 by Fremy, who named them sulphammonates. Their sulphonic constitution was made evident by Claus and Koch in 1869, and their nitrilic constitution by Berglund in 1875, when they received the name of nitrilosulphonates. Finally, Raschig rendered the constitution of these salts still more

certain in 1887. These chemists, it should be mentioned, added nothing to the experimental facts concerning the nitrilosulphates which Fremy had made known, but Claus and Koch determined the nature of the 'sulphazidates,' salts derived from Fremy's 'neutral sulphazotates' by hydrolysis; Raschig proved the constitution of the last-named salts, which by sulphonation become the sulphammonates, and Berglund established the constitution of the 'sulphamidates' into which the sulphammonates are transformed by hydrolysis, all the experimental inter-connections of these salts, here relied on, having been ascertained by Fremy himself. The recognition of the constitution of the nitrilosulphates by Fremy was a moral impossibility, for their discovery had come, so to say, much before its time.

Name.—The reason for the substitution of the name nitrilosulphates for that of nitrilosulphonates, chosen for these substances by Berglund, has been stated on a former occasion (Trans., 1896, **69**, 1634). As nitriles they are sulphates—nitrilosulphates therefore. Suitable alternative names are aminetrisulphonates and trisulphamates.

Preparation.—Ammonium nitrilosulphate, $4NH_3,3SO_3$, cannot be obtained by the union of ammonia with sulphur trioxide, for that results in the production of the imidosulphates, which are not resolvable by heat into nitrilosulphate and ammonia, since the less ammoniated $\frac{2}{3}$-normal salt, instead of breaking up in this way, boils freely at about 355° under reduced pressure, with very little decomposition and no production of nitrilosulphate (Trans., 1892, **61**, 947). Nitrilosulphates are only to be prepared by sulphonation of hydroximidosulphates. Fremy made known two ways in which this can be accomplished, of which, however, only one admits of general application. This is to treat the hydroximidosulphate with sulphur dioxide in presence of a base, a process which resolves itself in practice into treating the corresponding nitrite in this way, since the hydroximidosulphate has itself to be prepared by a similar sulphonation of the nitrite. The other way of preparing nitrilosulphates by sulphonation is to add a nitrite to an excess of solution of a pyrosulphite, when in the case of the potassium salt, the nearly insoluble nitrilosulphate soon separates. Other nitrilosulphates, being more soluble, can hardly be obtained directly in this way, but, as Fremy has shown, a solution of the ammonium salt thus prepared, very impure though it will be, can be made to yield potassium nitrilosulphate by double decomposition.

Ammonium Salt.

Nothing has been done concerning this interesting salt, $N(SO_3NH_4)_3,2H_2O$, since Fremy described it, but as its existence has been ignored since the time of the publication of its discovery until

now, we hold it important to again introduce some account of it derived from Fremy's memoir (*Ann. Chim. Phys.*, 1845, [iii], **15**, 408) into chemical literature. In presence of a large excess of ammonia, a concentrated solution of ammonium nitrite is submitted to the action of a current of sulphur dioxide until abundant precipitation of crystals has occurred in the solution kept sufficiently cool. The washed and dried salt gave Fremy the following numbers on analysis, indicating the presence of one molecular proportion of water of crystallisation :

	Sulphur.	Nitrogen.	Hydrogen.
$N_4H_{14}S_3O_{10}$ ...	29·45	17·18	4·29
Found	30·2	15·7	4·5

Since the potassium nitrilosulphate contains 2 mols. of water, it is probable that the ammonium salt contains the same, and that when Fremy determined the sulphur the salt had, like the sodium salt, lost some of its water during its stay in the desiccator. We write, therefore, the formula of the salt, $N(SO_3NH_4)_3,2H_2O$.

Ammonium nitrilosulphate separates in minute crystals which have only a slight taste, and are somewhat sparingly soluble in water, but so much more so than the potassium salt that Fremy suggested that its solution might be used as a qualitative reagent for potassium salts. It is not volatilised by heat, but is decomposed into sulphate. It is a very unstable salt, being liable in the solid state to decompose (hydrolyse) suddenly with a hissing sound, charring paper in contact with it. We have already announced (Trans., 1900, **77**, 689) our success in converting ammonium nitrite into hydroximidosulphate by a method of sulphonation which, carried farther, gave Fremy the nitrilosulphate.

Ammonium nitrilosulphate has the interest attached to it of being one more compound of ammonia with sulphur trioxide to be added to those recognised. There are six such compounds :

(1)	$NH_3,2SO_3$	=	$HN(SO_3H)_2$
(2)	NH_3,SO_3	=	$H_2N\,SO_3H$
(3)	$4NH_3,3SO_3$	=	$N(SO_3NH_4)_3$
(4)	$3NH_3,2SO_3$	=	$HN(SO_3NH_4)_2$
(5)	$4NH_3,2SO_3$	=	$(NH_4)N(SO_3NH_4)_2$
(6)	$2NH_3,SO_3$	=	$H_2N\,SO_3NH_4$

Of these, the second is amidosulphuric acid, and the sixth its ammonium salt (Trans., 1896, **69**, 1634); the first is imidosulphuric acid, known only in unstable solution (Trans., 1892, **61**, 945); the fourth is its $\frac{2}{3}$-normal ammonium salt (parasulphatammon of Rose); and the fifth, polymeric with the sixth, is its normal ammonium salt (sulphatammon of Rose ; Trans., 1892, **61**, 946); and the third is ammonium nitrilosulphate here described. These six compounds can all be

derived the one from the other, backwards as well as forwards, except the nitrilosulphate, which cannot be reformed from the others although itself the most convenient source of them. Nitrilosulphuric acid would be the seventh of these compounds, heading the column as $NH_3,3SO_3$, if it could exist in the free state.

Potassium Salt.

The potassium salt, $N(SO_3K)_3,2H_2O$, is familiar to those who have occupied themselves with the study of Fremy's sulphazotised salts, being one of the most insoluble of potassium salts, even more so than the perchlorate (Fremy). It forms slender needles of pearly lustre, which in crystallising fill its mother liquor. The work of later investigators has added nothing to the account of it given by Fremy, except that the crystals are rhombic (Raschig and Fock).* His analyses gave results which agree well with those calculated for the true composition of the salt, though not with his own formula for it. By preference, he prepared it by passing sulphur dioxide into a solution, not too concentrated, of the nitrite and the hydroxide. With the neglect of details characteristic of his celebrated memoir, he fails, however, to mention the essential potassium hydroxide. Probably, on account of this, later workers have only made use of his other process, which consists in mixing solutions of the nitrite and pyrosulphite.

Sodium Salt, $N(SO_3Na)_3,5H_2O$.

A strong solution of sodium pyrosulphite poured upon solid sodium nitrite furnished Raschig (*Annalen*, 1887, **241**, 180, 229) with a useful solution of the nitrilosulphate, although it contained much hydroximidosulphate, sulphite, and unchanged nitrite ; sodium hydroxide he represented also to be present, but that could not have been the case (Trans., 1900, **77**, 675). We have found that instead of 3 mols. of pyrosulphite, which was the quantity used by Raschig, to 2 mols. of nitrite, at least 4 mols. must be taken if most of the hydroximidosulphate is to be sulphonated.† By preparing from the carbonate (using this in hydrated crystals, along with only half its weight of water, and saturating with sulphur dioxide) a fresh and pure solution of pyrosulphite as concentrated as possible, pouring this solution upon the nitrite dis-

* Misled by the faulty translation in the *Annalen* (1845, **56**, 342) of Fremy's paper, Claus and Koch supposed that he had said that red fumes were evolved when the salt is heated. Fremy's statement is that the salt does not evolve red fumes, which is correct.

† Claus and Koch found it best to take still more pyrosulphite when working with the potassium salts (*Annalen*, 1869, **152**, 336), and they were right, for in the case of that insoluble nitrilosulphate, great excess of sulphite did not matter ; here it does.

solved in its own weight of water, 1 mol. of nitrite to every 2 mols. of carbonate taken, and shaking the flask in cold water for a short time to moderate the rise of temperature, a solution is obtained which will in an hour or two deposit a small quantity of sparkling crystals of the nitrilosulphate, and give a further amount when it is evaporated over sulphuric acid. The equation $NaNO_2 + 2Na_2S_2O_5 = N(SO_3Na)_3 + Na_2SO_3$ represents the change, but this would take many days to become complete, long before which time the nitrilosulphate would have all decomposed. In the mixed solution only a few hours old, some hydroximidosulphate, as well as nitrite, is still present.

The only satisfactory method of preparing sodium nitrilosulphate is a slightly modified form of that employed by us to get the imidosulphate (Trans., 1892, 61, 954). In that process, which is, after all, only a development of Fremy's method of preparing the ammonium salt, the nitrilosulphate is prepared and at once allowed to hydrolyse into imidosulphate, whereas in the present case its hydrolysis is to be prevented. There, a moderately concentrated solution met the end in view, whilst here the greatest possible concentration is wanted, because evaporation of the solution afterwards, although sometimes successful, is a very uncertain operation, in consequence of the short existence which can be assured to the nitrilosulphate. A solution therefore is prepared of 2 mols. of nitrite to 3 mols. of carbonate, so concentrated that the water is scarcely more than twice the weight of the anhydrous carbonate (for example, 10 grams of nitrite, 8·5 grams of hot water, and 62·2 grams of carbonate crystals). Sulphur dioxide is passed rapidly into the solution in a flask continuously shaken. When, after a time, the solution grows hot, the flask is immersed in cold water, and when it thickens, through temporary separation of acid carbonate, vigorous shaking of the flask is to be maintained without intermission. As the quantity of the acid carbonate suspended in the warm solution (50—60°) lessens, the rate of current of the sulphur dioxide should be reduced and the action of the solution upon litmus paper closely watched. At the moment the solution reddens the litmus, the entrance of more sulphur dioxide must be stopped, for should acidity to lacmoid paper also be reached, through the addition of much more sulphur dioxide, the nitrilosulphate will at once hydrolyse into the imidosulphate. During the final slow sulphonation, the solution will generally grow cold enough to begin to deposit small crystals of the nitrilosulphate, recognisable by their brilliant lustre; these will increase largely in quantity at the temperature of the air. Without waiting too long, it is safer to add two or three drops of concentrated solution of sodium hydroxide, sufficient to render the solution faintly alkaline to litmus. It is possible to get more of the salt by evaporating the mother liquor over sulphuric acid.

That the reaction proceeds sharply in accordance with the following equation, is known from the quantity of imidosulphate which such a solution can be made to furnish:

$$2NaNO_2 + 3Na_2CO_3 + 8SO_2 = 2N(SO_3Na)_3 + Na_2S_2O_5 + 3CO_2.$$

In consequence, however, of the great solubility of this nitrilosulphate, the crystals obtained amount to barely more than one-fifth of the total quantity; still, even that is 120 per cent. of the weight of nitrite taken. The crystals hold 21·8 per cent. of water, or $5H_2O$. Of this quantity, it has twice been possible to remove 15·5 per cent. by exposing the salt in a vacuum over sulphuric acid, after which the salt has hydrolysed, and thereby fixed the rest of the water. The production of the unused pyrosulphite, shown in the above equation, is necessary for the safe and prompt sulphonation of all the hydroximidosulphate.

Sodium nitrilosulphate crystallises in short, thick prisms which melt when heated and decompose in their water of crystallisation into sulphates. The crystals cannot be long preserved under any circumstances, soon suffering decomposition and becoming opaque and acid, even in their own mother liquor after it has been made alkaline. That is, the sodium salt is more unstable than the potassium salt. It is neutral to litmus, and must be soluble in about its own weight of water, to judge from the amount of it left in the mother liquor in its preparation, although here, no doubt, the pyrosulphite also in solution will affect its degree of solubility.

For analysis, it was drained on the tile after washing with a little strong ammonia-water, in which it is less soluble than in water. Partial water determinations have already been referred to.

	Sulphur.	Sodium.	Nitrogen.
$N(SO_3Na)_3,5H_2O$	23·24	16·71	3·39
Found	23·05	16·54	—
„	22·96	—	3·64
„	23·25	16·68	—
„	23·17	—	3·45
„	—	16·55	—

Double Salts.

Potassium Sodium Nitrilosulphate, $N(SO_3)_3K_2Na$.—Raschig obtained this salt by adding a solution of potassium chloride gradually to a crude solution of sodium nitrilosulphate (p. 1096). We have obtained the same salt, which is like the sodium salt in appearance and like the potassium salt in being nearly insoluble. According to Raschig, it is anhydrous, and occurs either as a sparkling sand or in hard crystals the size of pinheads and of adamantine lustre.

Barium Salts.—By dissolving the sodium salt in a strong solution of barium chloride rendered faintly alkaline with ammonia, a flocculent precipitate is obtained which becomes dense and crystalline on standing. It is sparingly soluble in water and very unstable. It probably contains sodium, but we have not analysed it. Fremy obtained barium ammonium and barium potassium salts, which he could only analyse imperfectly because of their instability. They resembled the barium sodium salt, and from the results of his analyses appear to have been two-thirds barium and one-third ammonium or potassium salt, with water of crystallisation.

Lead Salts.—According to Fremy, very unstable lead salts containing potassium or ammonium are obtainable.

CXVIII.—*Ammonium and other Imidosulphites.*

By Edward Divers and Masataka Ogawa.

The fact of the existence of ammonium imidosulphite as a product of the decomposition of the amidosulphite by very gentle heating, $2NH_2{\cdot}SO_2{\cdot}NH_4 = NH_3 + NH(SO_2NH_4)_2$, was brought before a meeting of the Society last session (Proc., 1900, **16**, 113). The present paper consists of a fuller account of this salt and other imidosulphites than could then be given.

Ammonium amidosulphite, from which the imide salt is derived (Trans., 1900, **77**, 327), is readily formed by the union of sulphur dioxide and ammonia, but is so unstable as to be largely decomposed by the unavoidable heating it suffers when these gases come together, unless cooled ether be used as their solvent. On keeping the dry salt at a temperature of about 35°, its decomposition goes on, and ammonia escapes for some hours. There is left a mottled orange mass of waxy consistence already described in the earlier paper (*loc. cit.*, p. 333), which is difficult to attack with solvents other than water, because it adheres very firmly to the vessel and must not be exposed to the air during treatment. By protracted digestion with successive portions of 90 per cent. spirit, aided by scraping with a pointed glass rod and vigorous shaking, it can, however, be nearly all dissolved up, although only very sparingly soluble. The first portions of the solution are coloured, and contain a salt, the presence of which interferes with the preparation of the imidosulphite from them. The later colourless extracts yield the imidosulphite when they are evaporated in the vacuum desic-

cator, but not quite pure. Much better results are got by beginning the treatment with warm 95 per cent. spirit, used in successive portions, until the residue is a colourless powder, and only then resorting to the 90 per cent. spirit and carrying on the digestion at about 50°. The solution thus obtained deposits almost pure imidosulphite as it cools, and the mother liquor can be used with advantage again and again to dissolve out more of the salt, although in that case the crystals which separate are somewhat impure. These can be purified by washing with absolute alcohol containing much ammonia to dissolve out the foreign salt (more soluble in presence of ammonia), and then dissolving up in warm 90 per cent. spirit and recrystallising. The original mother liquor yields more imidosulphite, but impure, when it is either artificially cooled (as by ice and salt) or is evaporated in the desiccator. This impure salt can be purified in the way just described. All the ammonium imidosulphite is finally washed with ammoniacal alcohol, drained on a porous tile under close cover, and dried in a desiccator over potash. The quantity of pure salt actually obtained in this way approaches that of a fourth only of the weight of decomposed amidosulphite taken, but the total production of imidosulphite will no doubt prove to be very much greater.

Analysis.—The salt, 0·4240 gram, distilled with potash, yielded ammonia, 0·0817 gram, and then, after heating for some time in a tube with hydrochloric acid under pressure and again distilling with potash, 0·03755 gram more ammonia. Simple distillation with potash of 0·4912 gram of another portion of salt gave 0·0939 gram of ammonia, and then, after oxidation by means of bromine followed by hydrochloric acid and potassium chlorate, 1·2886 grams of barium sulphate. The calculated and found percentages are :

	Ammonia nitrogen.	Imide nitrogen.	Total nitrogen.	Sulphur.
$NH(SO_2NH_4)_2$ ...	15·64	7·82	23·46	35·75
Found	15·86	7·29	23·15	—
„	15·74	—	—	36·02

It will be seen that the analysis establishes, not only the composition of the salt to be $3NH_3,2SO_2$, but also its imide constitution.

Properties.—It occurs in minute, micaceous needles. Heated very slowly in a tube, it soon begins to decompose into volatile substances and a residue of sulphur, ammonium sulphate, and the $\frac{2}{3}$ normal ammonium imidosulphate, $[NH(SO_3NH_4)_2]$. Even when the temperature is raised to 150°, no fusion takes place. The sublimates which form during the heating begin to appear at about 80°, and consist apparently of ammonium pyrosulphite, $[(NH_4)_2S_2O_5]$, and the unchanged

imidosulphite, $[(NH_4)_2S_2O_4NH]$. The salt is insoluble in alcohol, and in this respect is unlike ammonium amidosulphite, which is very soluble as ethyl ammoniumsulphite and ammonia. The salt is only moderately deliquescent and, freshly prepared, is neutral to litmus.* It has a mild, unpleasant, sulphurous taste, which distinguishes it from the salt occurring with it, more freely soluble than it in 95 per cent. spirit, and already referred to.

It is freely soluble in water, but slowly decomposes into thiosulphate and amidosulphate. This change beginning at once, the solution gives all the reactions of a thiosulphate. It goes on also in presence of hydrochloric acid, which when hot hastens its completion. Barium thiosulphate has been prepared from the solution, and amidosulphuric acid and ammonium amidosulphate also obtained from it. Quantitative determinations of the sulphur, sulphur dioxide, and amidosulphate formed on boiling with hydrochloric acid gave results in agreement with the following equation:

$$2NH(SO_2NH_4)_2 + 2HCl = 2NH_2{\cdot}SO_3NH_4 + 2NH_4Cl + SO_2 + S$$

in which the SO_2 and S represent decomposed thiosulphuric anhydride.

Potassium Imidosulphite.—It has already been stated when detailing the analysis of the ammonium salt, that that salt yields just two-thirds of its nitrogen as ammonia when boiled with potassium hydroxide in aqueous solution. In accordance with this fact, it has been found that potassium imidosulphite is obtained when, to the ammonium salt dissolved in 70 per cent. spirit, alcoholic potash is added until the solution just renders red litmus paper permanently blue on exposure to air. The salt soon separates as minute, micaceous crystals firmly adherent to the glass. After repeated washing with absolute alcohol, the salt has been found to remain alkaline to litmus, quite possibly, however, because of the presence of a trace of tripotassium salt, as happens in the case of imidosulphates. The imidosulphite unlike the corresponding potassium imidosulphate, $NH(SO_3K)_2$, is very soluble in water, and its solution gives the imidosulphite reactions of the ammonium salt. It has, too, the sulphurous taste of that salt. In the analysis, nitrogen was determined by the combustion method, sulphur by oxidation, as in the analysis of the ammonium salt, and potassium by ignition with sulphuric acid, with the following results:

* As first obtained by us last year and then described, the salt had an acid reaction and was exceedingly deliquescent; but as it showed a deficiency in ammonia (22·2 instead of 23·5 per cent.), and as its potassium derivative was not acid, we indicated our expectation that when obtained in a purer state the salt would prove to differ somewhat in properties from what we had then found.

	Potassium.	Nitrogen.	Sulphur.
$NH(SO_2K)_2$	35·29	6·33	28·96
Found	35·17	6·74	28·88
„	—	6·93	—

Barium Ammonium Imidosulphite.—When the orange mass of decomposed amidosulphite is dissolved in water and mixed with baryta water in such quantity as to leave undecomposed some of the ammonium imidosulphite it contains, the filtered solution when concentrated in the desiccator deposits the double salt in minute, micaceous crystals. Only barium and sulphur were determined. The results agree with those calculated for $Ba(SO_2NHSO_2NH_4)_2$.

	Barium.	Sulphur.
$BaN_4H_{10}S_4O_8$	29·85	27·89
Found	29·94	26·90

In the Proceedings (1900, 16, 104), the existence of this salt was indicated, but by mistake it had been taken to be a salt of the acid $N_2H_4S_2O_8$, and was accordingly formulated as $Ba(N_2H_3S_2O_3)_2,2H_2O$. It is soluble in water, and its solution behaves as that of an imidosulphite, being precipitable by baryta ($N_2H_4S_2O_3$ salts are not), and besides at once gives off ammonia when moistened with potassium or barium hydroxide solution.

The treatment of the orange mass of decomposed ammonium amidosulphite with 95 per cent. spirit as a preliminary to dissolving out the main quantity of imidosulphite with 90 per cent. spirit, yields yellow, alcoholic solutions, which on evaporation in the desiccator deposit crystals which are short, thick prisms almost cubical in appearance and about 2 mm. across. They are thus quite unlike the minute, micaceous needles of ammonium imidosulphite. They are yellow, but the colour is adventitious. They can be purified and rendered white by putting them into 95 per cent. spirit and then almost saturating this with ammonia, while the containing flask is kept immersed in cold water. In this alcoholic ammonia, they are very sensibly soluble. The solution is decanted, and the treatment repeated until only a small quantity of white, powdery salt remains, principally imidosulphite. The solutions left for a while in open flasks, and then exposed in the desiccator over sulphuric acid, lose most of the ammonia, and the crystals reform from the solution. Washed with alcohol, they are left quite colourless. The mother liquors evaporated in the desiccator yield crude, yellow crystals again, which can be recrystallised from alcoholic ammonia as before.

These crystals are recrystallisable without change, and have also

been prepared by us in two successive winters, yet they give analytical results which are closely concordant with the remarkable empirical formula $4NH_3,5SO_2$ or $N_4H_{12}S_5O_{10}$.

	Nitrogen.	Sulphur.
$N_4H_{12}S_5O_{10}$	14·43	41·24
Found in 1900.....	14·11	41·14
„ „	14·36	40·02
„ in 1901	14·02	41·02
„ „	14·40	—

These crystals are neutral and have a bitter taste, not a sulphurous one. They are freely soluble in water, and very deliquescent. The solution is unstable, and in some of its reactions greatly resembles that of ammonium imidosulphite. With potassium hydroxide, the salt evolves ammonia at once, but analyses of potassium salts prepared from it in 70 per cent. alcoholic solution have given discordant results. A striking difference from an imidosulphite is that its fresh solution gives no barium precipitate, even in presence of ammonia. Also that in freshly prepared solution, it does not decolorise iodine solution, and only slowly decolorises cold acid permanganate. It also does not give the ferric chloride coloration of a thiosulphate, which the imidosulphite does give. Its solution becomes very acid after a time, and then smells much more strongly of suphur dioxide than a similar solution of imidosulphite. The crystalline matter having nearly the composition expressed by $9NH_3,8SO_2$, mentioned in our paper on ammonium amidosulphite (Trans., 1900, 77, 334) we believe to have been the present salt mixed with imidosulphite and amidosulphate. On a future occasion, we hope to be in a position to report upon the constitution of the substance we have here described.

CXIX.—*Ethyl* sec. *Octyl Tartrate and its Dibenzoyl and Diacetyl Derivatives.*

By JOHN McCRAE.

DURING the course of an investigation of the monoacyl derivatives of tartaric esters (Frankland and McCrae, Trans., 1898, 73, 307), it was found that, no matter how large an excess of methyl tartrate was taken, the action of an acid chloride on it always led to the formation of a very large proportion of the diacyl compound. With diethyl tartrate, however, it was possible by using an excess of the ester to prevent the formation of the diacyl derivative, and so obtain the monoacyl compound. In order to ascertain whether it would be easily possible to

prepare monoacyl derivatives of a tartaric ester containing an alkyl group high in the series, the following investigation was undertaken. It was originally intended to prepare dioctyl tartrate and investigate the action of acid chlorides on it, but early in the course of the work an easy method of obtaining ethyl octyl tartrate was discovered, and, so far, only this and its diacyl products have been examined. The work is being carried further, in order to realise the original intention.

The results obtained do not indicate that the introduction of the octyl group in place of the ethyl exerts any retarding influence on the production of diacyl derivatives.

For the purpose of obtaining a tartaric ester with an alkyl group of high molecular weight, the most suitable alcohol to use appeared to be octyl alcohol. *sec.*Octyl alcohol (methyl-*n*-hexylcarbinol) is a commercial article, and was adopted in the experiments. When the work was started, the results of Marckwald and McKenzie (*Ber.*, 1901, **34**, 469) had not been published, and it was believed that this alcohol was a homogeneous material. Marckwald and McKenzie have shown that the substance is not pure, but consists of a mixture of a lævorotatory and an inactive compound. Until the active component present in the octyl alcohol is more definitely characterised, it would be superfluous to enter into a discussion of the possible isomerides which may be formed from a combination of the two active compounds.

As the octyl alcohol used throughout has been of the same composition, the results obtained for the different compounds are strictly comparable with each other (Landolt, "Optical Activity and Chemical Composition," p. 121).

Experimental.

The octyl alcohol was obtained from Kahlbaum, and had the same rotation as that employed by Marckwald and McKenzie, namely, $\alpha_D = -17'$ ($l = 4$) (compare also Patterson, this vol., p. 490).

Fifteen grams of dried tartaric acid were heated in a sealed tube with 60 grams of distilled octyl alcohol for 3 days at 140—160°. On distilling the mixture under diminished pressure, the excess of alcohol and the water passed over at a comparatively low temperature, and at 220—240°, under 15 mm. pressure, a substance distilled which was probably dioctyl tartrate. Much decomposition took place, and the yield was very poor.

On account of the insolubility of tartaric acid in octyl alcohol, the hydrochloric acid method could not be used directly.

Purdie and Marshall (Trans., 1888, **53**, 391) have shown that it is possible to transform one ester into another by the action of an

alcohol, and it was thought possible that such a transformation might be effected if a tartaric ester could be obtained which is soluble in octyl alcohol. Meanwhile, Patterson and Dickinson (this vol., p. 280) had proved that a reciprocal transformation of methyl and ethyl tartrates is possible with ethyl and methyl alcohols and hydrochloric acid. This method was tried, and it has been found that after a single treatment of ethyl tartrate and octyl alcohol in proper proportions with hydrochloric acid, pure ethyl octyl tartrate can be produced.

Ethyl Octyl Tartrate.

Fifty grams of diethyl tartrate are dissolved in 200 grams of octyl alcohol and the solution saturated with dry hydrochloric acid in the cold. After standing for 24 hours, the hydrochloric acid is extracted under diminished pressure and the water and ethyl alcohol, as well as the excess of octyl alcohol, are distilled off. The residue is then distilled, still under diminished pressure, and the fraction passing over between 170° and 205° under 15 mm. pressure is collected. As the boiling points of diethyl and ethyl octyl tartrates do not lie far apart, it is not easy to separate them by fractional distillation, and the distillate thus obtained constantly contains some unchanged diethyl tartrate. This is best got rid of by shaking with water, which dissolves (and hydrolyses) the ethyl compound, but does not dissolve or decompose the ethyl octyl derivative. After washing three or four times with water, the oil is dried as completely as possible over sulphuric acid in a vacuum. It is then distilled under diminished pressure once or twice (b. p. 200—202° under 15 mm. pressure), or until the rotation is constant. It was generally found that the rotation did not alter after two distillations.

In one preparation, some of the excess of octyl alcohol which had been distilled off was washed with water, then redistilled, and the rotation of the fraction boiling at 178° was found to be $\alpha_D = -18'$ ($l = 4$), as compared with $\alpha_D = -17'$ found for the original alcohol. There is here no evidence of a variation in the rate of esterification of the constituents of the alcohol, but it must be remembered that the process was carried out very differently from the method used by Marckwald and McKenzie.

Various preparations of ethyl octyl tartrate gave the same rotation, namely, $+5°22'$ in a 66·04 mm. tube at 16°.

It is a viscous, colourless oil with a decidedly rancid odour.

0·1940 gave 0·4108 CO_2 and 0·1548 H_2O. C = 57·75 ; H = 9·07.
0·1195 „ 0·2537 CO_2 „ 0·0950 H_2O. C = 57·90 ; H = 8·83.
$C_{14}H_{26}O_6$ requires C = 57·93 ; H = 8·97 per cent.

A determination of the ethoxy-group by Zeisel's method gave the following result:

0·1490 gave 0·1039 AgI. $C_2H_5 = 8·61$.

$C_{14}H_{26}O_6$ requires $C_2H_5 = 10·00$ per cent.

The density and rotatory power were then determined at various temperatures, and the following numbers were obtained:

d 15°/4° = 1·0664. d 30°/4° = 1·0533. d 45°/4° = 1·0402.
d 60°/4° = 1·0277. d 79·8°/4° = 1·0100.

Rotation of ethyl octyl tartrate.

(Length of polarimeter tube = 66·04 mm.)

Temperature. $t°$.	Observed rotation.	Density at $t°$.	$[\alpha]_D$.	$[M]_D$.
16	+5°22′	1·0655	+7·63°	+22·13°
21·5	5 29	1·0608	7·83	22·71
41·5	6 27	1·0433	9·36	27·14
50	6 56	1·0360	10·13	29·38
62	7 23	1·0259	10·89	31·58
71	7 41	1·0177	11·43	33·15
98	8 21	0·9937	12·72	36·89

Ethyl Octyl Dibenzoyltartrate.

By heating together ethyl octyl tartrate and benzoyl chloride at 100°, reaction took place—rather more sluggishly than with diethyl tartrate—and from the high negative rotation of the resulting product it was evident, in analogy with the high negative rotation of diethyl dibenzoyltartrate (Frankland and Wharton, Trans., 1896, 69, 1586), that much diacyl ester was formed even when no excess of acid chloride was used.

The monoacyl diethyl tartrates were obtained in the solid state, and could be separated from the diacyl derivatives by repeated crystallisation; as no acyl derivative of ethyl octyl tartrate has been obtained in the solid state, and, further, as they seem to decompose on heating, so that they cannot be distilled, the task of separating the mono- from the di-acyl compound seemed hopeless, and the preparation of the monoacyl derivatives was abandoned.

As has been noticed, ethyl octyl dibenzoyltartrate is constantly formed when benzoyl chloride is treated with excess of ethyl octyl tartrate, and, on the other hand, the substance is not obtained pure even when a very large excess of acid chloride is used, on account of the incompleteness of the reaction.

The method which ultimately led to its isolation was as follows: One hundred grams of benzoyl chloride were heated under a reflux condenser in a water-bath, and 36 grams of ethyl octyl tartrate were slowly dropped in with continual shaking. The heating was continued for 4 days, when no more hydrochloric acid was evolved. The product was washed with water, and then with sodium carbonate solution. Most of the benzoyl chloride was thus removed, but as this is not easily completely destroyed by water, it was found to be necessary to dissolve the oil in ether and shake the ethereal solution with sodium carbonate solution for 3 or 4 days, occasionally renewing the carbonate solution. The ethereal solution was separated, dried as completely as possible over ignited potassium carbonate, and, after filtering, the ether was distilled off. The last trace of ether was expelled by warming the ester in the steam-oven, then placing it in an exsiccator, and exhausting the air. A yellowish oil was thus obtained weighing 56 grams. The rotation of this at 16·5° was found to be $-32°16'$ in a 66 mm. tube. The substance is easily soluble in the common organic solvents; it is quite insoluble in water, which appears to have no appreciable hydrolysing action on it. Heated in a vacuum, it undergoes decomposition, and benzoic acid (recognised by its melting point) was found in the distillate.

For its purification, precipitation by water from an alcoholic solution was adopted. The oil was dissolved in hot absolute alcohol and water was added until there was just a permanent opalescence at the high temperature. It is advisable not to boil the alcoholic solution, as an interchange of alkyl groups (ethyl for octyl) might possibly then take place, although this has not been actually observed. On cooling, the solution deposited an oil, the colour of which was not so intense as before. The oil was dissolved in ether, and the ethereal solution dried and treated as before. The rotation of the product had then risen to $-33°20'$ at 15·5° in the same tube. After repeating this process of purification, the rotation had further increased to $-34°47'$ at 15·5°, and the next purification led to the production of a substance with rotation $-35°55'$ at 11° in the 66 mm. tube, after which the rotation was not sensibly altered by further treatment.

The whole of the substance in the alcoholic solution was not precipitated with water, and the various residues were combined and the whole separated by the addition of more water. The oil was extracted with ether, and after drying with ignited potassium carbonate and evaporating off the ether, the residue had a rotation of $-29°56'$ in the 66 mm. tube at 14°. This oil probably consisted for the most part of ethyl octyl dibenzoyltartrate, but whether the admixture was unchanged ethyl octyl tartrate or the monobenzoyl derivative (which presumably has a higher dextrorotation than the

simple ester—see McCrae and Patterson, Trans., 1900, 77, 1107) was not determined.

Another preparation had the same rotation.

The compound has only been obtained as a clear, almost colourless, viscous oil. It was suspended in boiling liquid air and at once set to a hard, glassy mass which melted on regaining the ordinary temperature. It has been kept for more than 6 months under water, but shows no sign of solidifying.

0·2542 gave 0·6245 CO_2 and 0·1486 H_2O. C = 67·00 ; H = 6·50.
$C_{28}H_{34}O_8$ requires C = 67·47 ; H = 6·83 per cent.

The influence of temperature on the density and on the rotation has been determined.

The density observations actually made were :

d 19°/4° = 1·0884.	d 38·5°/4° = 1·0728.
d 61°/4° = 1·0533.	d 78°/4° = 1·0396.

Rotation of ethyl octyl dibenzoyltartrate.

(Length of polarimeter tube = 66·04 mm.)

Temperature. $t°$.	Observed rotation.	Density at $t°$.	$[\alpha]_D$.	$[M]_D$.
10·8	−35°45′	1·0956	−49·41°	−246·0°
24·2	−35 19	1·0845	−49·31	−245·6
38	−34 50	1·0729	−49·16	−244·8
47·5	−34 20	1·0649	−48·81	−243·1
54	−34 2	1·0595	−48·64	−242·2
67	−33 31	1·0488	−48·39	−241·0
79	−32 19	1·0386	−47·12	−234·7
88	−31 27	1·0313	−46·18	−230·0
99	−30 17	1·0220	−44·88	−223·5

Ethyl Octyl Diacetyltartrate.

Acetyl chloride reacts energetically on ethyl octyl tartrate, just as it does on diethyl tartrate. Diethyl monoacetyl tartrate is extremely difficult to separate from the diacetyl derivative, in spite of the fact that the latter can easily be obtained in the solid form (McCrae and Patterson, *loc. cit.*). As ethyl octyl diacetyltartrate has not been obtained in the solid state, it appeared at the outset a hopeless task to try to prepare the monoacetyl derivative, and consequently no attempts have been made in this direction.

To obtain the diacetyl compound, 30 grams of ethyl octyl tartrate were slowly run into 50 grams of acetyl chloride heated in a water-

bath under a reflux condenser. The heating was continued until there was no further evolution of hydrochloric acid—which may require so long as 24 hours. The resulting product was poured into water and treated as described for the dibenzoyl compound.

The oil produced in this way in one preparation had a rotation of + 2°30′ in a 66 mm. tube at 14°. For the purification, the same method (separation from alcoholic solution by means of water) has been adopted as for the dibenzoyl derivative. After three separations it was found that the rotation was constant (α_D = 2°58′, l = 0·66, t = 20·5°). Another preparation had a rotation of 2°55′ at 20° in the same tube.

Ethyl octyl diacetyltartrate is a clear, viscous oil with a very slight rancid odour. It cannot be distilled, as on heating much above 100° it undergoes decomposition.

0·1772 gave 0·3728 CO_2 and 0·1148 H_2O. C = 57·38 ; H = 7·20.
$C_{18}H_{30}O_8$ requires C = 57·75 ; H = 8·02 per cent.

The density and rotation have been determined at various temperatures.

d 18·1°/4° = 1·0554. d 31·5°/4° = 1·0429.
d 49·2°/4° = 1·0271. d 70·5°/4° = 1·0071.

Rotation of ethyl octyl diacetyltartrate.

(Length of polarimeter tube = 66·04 mm.)

Temperature. t°.	Observed rotation.	Density at t°.	$[\alpha]_D$.	$[M]_D$.
18·5	+2°56′	1·0553	+4·20°	+15·71°
44	3 14	1·0317	4·63	17·32
61	3 36	1·0160	5·37	20·08
81·5	4 14	0·9968	6·43	24·05
100	4 41	0·9800	7·23	27·04

Conclusions.

From the results obtained with ethyl octyl tartrate, it is evident that the rotation increases with rise of temperature at about the same rate as that of diethyl tartrate does :

	$[\alpha]_D$	$[\alpha]_D^{100}$
Diethyl tartrate (Pictet).....	7·66°	13·29°
Ethyl octyl tartrate.....	7·78	12·75

If we compare the rotations of ethyl octyl tartrate and its derivatives with those of diethyl tartrate, we notice a striking similarity, in agreement with the rule suggested by Guye (Guye and Babel, *Arch.*

Sci. phys. nat. Geneva, 1899, iii, 7, 114; and Guye, this vol., p. 476), namely, that substitution effected sufficiently far removed from the asymmetric carbon atom scarcely modifies the rotatory power.

Using the diethyl compounds as starting point, the following table shows that the replacement of a methylene hydrogen atom of one of the ethyl groups by *n*-hexyl gives rise to only a comparatively small change in the molecular rotation.

	$[M]_D^{20}$	$[M]_D^{100}$
Diethyl tartrate*	+15·78°	+27·38°
Ethyl octyl tartrate	+22·55	+37·17
Diethyl diacetyltartrate†	+9·9	+18·26
Ethyl octyl diacetyltartrate.....	+15·80	+27·04
Diethyl dibenzoyltartrate‡	−247·1	−251·6
Ethyl octyl dibenzoyltartrate	−245·8	−222·8

The influence of temperature on the rotatory power of all these compounds is the same, namely, with rise of temperature the dextrorotation increases (or the lævorotation diminishes).

Frankland and Wharton (*loc. cit.*) have found that the lævorotation of diethyl dibenzoyltartrate increases with rise of temperature up to a maximum reached at about 60°, and thereafter it progressively decreases. Allowing, therefore, for this anomaly, the influence of temperature on diethyl dibenzoyltartrate is the same as on the other tartrates mentioned, although the two numbers given would appear to contradict this. No corresponding anomalous behaviour has been observed with ethyl octyl dibenzoyltartrate, but attention may be directed to the observation that the rotation of both this and the diacetyl derivative is considerably more affected by change of temperature near 100° than it is at low temperature.

The expense incurred in the prosecution of this work has been defrayed by a grant from the Research Fund of the Chemical Society. I desire here to acknowledge my indebtedness for this, and also to express my thanks to Dr. Patterson for so kindly placing his Laurent polarimeter at my disposal.

The Yorkshire College,
Leeds.

* Pictet, *Jahresber.*, 1882, 856. † McCrae and Patterson (*loc. cit.*).
‡ Frankland and Wharton (*loc. cit.*).

CXX.—*The Aluminium-Mercury Couple. Part III. Chlorination of Aromatic Hydrocarbons in presence of the Couple. The Constitution of the Dichlorotoluenes.*

By Julius B. Cohen and Henry D. Dakin, the Yorkshire College.

Introduction.

The readiness with which the aromatic hydrocarbons undergo bromination in presence of the aluminium-mercury couple (Trans., 1899, **75**, 893) suggested a series of experiments on the chlorination of these hydrocarbons under similar conditions.

By passing dry chlorine into benzene in presence of a fragment of the couple, chlorination proceeds actively, the liquid becoming darker in colour whilst torrents of hydrochloric acid are evolved. The couple is only slightly attacked.

By interrupting the process when a certain increase in weight had been obtained, the different chlorination products from the monochlorobenzene to the hexachlorobenzene were, in turn, isolated. Where the products were solid, it was necessary to add carbon tetrachloride to keep the substance in solution during chlorination. Similar experiments were carried out with toluene.

The systematic study of the action of chlorine on toluene dates from the year 1866, when Beilstein and Geitner (*Annalen*, 1866, **139**, 331) discovered the action of chlorine on hot and cold toluene in producing substitution in the side-chain or nucleus, and showed at the same time that by the use of iodine—a halogen carrier first employed by Hugo Müller—substitution may be confined to the nucleus. Since then, the action of chlorine on toluene in presence of different "halogen-carriers" has been repeatedly investigated with the object of orienting the products formed.

The data which have thus been accumulated by different observers are very voluminous, but are so conflicting, that at the present time our knowledge of the products of this simple reaction is very indefinite.

It was in attempting to collect evidence of the constitution of the chlorine derivatives of toluene by reference to the work of previous observers that we first realised its unsatisfactory character and determined to make a complete study of the whole subject.

The conflicting nature of the evidence will be readily understood from the following brief summary.

Beilstein and Geitner (*loc. cit.*) and Beilstein and Kuhlberg (*Annalen*,

1869, **150**, 313; **152**, 224) in their first papers describe only one monochlorotoluene, whilst Hübner and Majert (*Ber.*, 1873, **6**, 790) announced the discovery of two, since identified as the ortho- and para-compounds. Beilstein and Kuhlberg (*Annalen*, 1869, **152**, 224) found one dichlorotoluene, which on oxidation gave a dichlorobenzoic acid, m. p. 201—202°. Curiously enough they appear to have overlooked the existence of a second isomer, although they obtained from the mixture a dichlorobenzylidene dichloride, $C_6H_3Cl_2 \cdot CHCl_2$, which gave an aldehyde, and, on oxidation, an acid, m. p. 128°.

Aronheim and Dietrich (*Ber.*, 1875, **8**, 1401), however, using molybdenum pentachloride as carrier, gave proofs of the existence of two dichlorotoluenes by separating the two dichlorobenzoic acids, m. p. 201° and 122°, by fractional crystallisation of the barium salts. This agrees substantially with the results of Beilstein and Kuhlberg. R. Schultz (*Annalen*, 1877, **187**, 260) repeated the work of the previous investigators, and by fractional crystallisation of the barium salts of the benzoic acids obtained compounds of the m. p. 201°, 126°, and 156°, and thus brought evidence of the existence of a third dichlorotoluene. The orientation of these compounds could only be determined with certainty after the pure dichlorobenzoic acids had been prepared. This work was carried out by Lellmann and Klotz (*Annalen*, 1885, **231**, 308), who prepared four of the six isomers, the whole number being subsequently completed by Wynne and Greeves (Proc., 1895, **11**, 151). As certain discrepancies appear in the results of various observers, we have also prepared the same series of acids and the combined results are tabulated below.

Melting points of dichlorobenzoic acids.

CH_3=1.	Lellmann and Klotz.	Wynne.	C. and D.	Other observers.
2·3	—	164°	163°	156° (Claus) *
2·4	158°	—	159—160	166° (Seelig)
2·5	153·5	152	153	
2·6	—	139	139—140	128° (Beilstein) 126·5° (Schultz) 132° (Claus)
3·4	201	202	200—201	
3·5	182	—	182·5—183	182° (Claus)

* Claus and Bucher (*Ber.*, 1887, **20**, 1621) obtained this acid by the action of bleaching powder or potassium chlorate and hydrochloric acid upon benzoic acid. It was then converted into a dichlorobenzene which was identified as the ortho-compound.

The melting points of Schultz's three acids are in fair agreement with those of the 3 : 4-, 2 : 4-, and 2 : 6-compounds, the only doubt existing

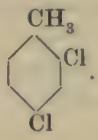
between the 2 : 3- and 2 : 4-compounds. But a later investigation of Seelig (*Annalen*, 1887, **237**, 129) on the action of chlorine on toluene in presence of ferric chloride or molybdenum chloride has introduced new features into the problem. He gives evidence only of a 2 : 4- and a 2 : 3-compound, no mention being made either of a 3 : 4- or a 2 : 6-compound. As this is much the most elaborate investigation on the subject, the evidence which he adduces may now be briefly reviewed.

According to Seelig, the 2 : 3- and 2 : 4-dichlorotoluenes which are formed may be separated by fractional crystallisation of their calcium sulphonates.

Each dichlorotoluene forms a crystalline dinitro-derivative, the 2 : 3-compound melting at 121° and the 2 : 4-compound melting at 101—102°.

Evidence of their constitution is derived by Seelig from the following facts :

(1.) The first products of chlorination consist of a mixture of ortho- and para-monochlorotoluenes. If either of these compounds is chlorinated, a mixture of the same two trichlorotoluenes results. Two of the chlorine atoms in these compounds will therefore be in positions 2 : 4.



The position of the third chlorine atom is determined as follows. Each of the trichlorotoluenes was converted into a dinitro-derivative, which was reduced to a diamino-compound. One of the diamino-compounds when heated with acetic anhydride forms an anhydro-base, and therefore contains the two amino-groups in the ortho-position. The second diamino-compound, on oxidation, yields a quinone and consequently has the two amino-groups in the para-position. The two diaminotrichlorotoluenes will be represented thus :



that is to say, the trichlorotoluenes have the chlorine atoms in the 2 : 3 : 4- and 2 : 4 : 5-positions.

This leaves a choice between the 2 : 3- ; 2 : 4- ; 2 : 5-, and 3 : 4-formulæ for the dichlorotoluenes.

Now if ortho- and para-monochlorotoluene are chlorinated so as to form dichlorotoluenes, Seelig found that the ortho-compound yields

two, an α- and β-dichlorotoluene, whereas the para-compound yields only one, namely, the β-compound. The β-compound, since it is derived from both ortho- and para-monochlorotoluene, must have the 2 : 4-formula, which Seelig confirmed by converting it into the 2 : 4-dichlorobenzoic acid, m. p. 158°, obtained by Lellmann and Klotz (*loc. cit.*). The constitution of the α-compound must lie between the 2 : 3- and 2 : 5-formula, since it is obtained from the *o*-monochlorotoluene. The α-compound yields on oxidation a dichlorobenzoic acid, m. p. 166°. This does not agree with the melting point of the 2 : 5-compound which Lellmann and Klotz had previously ascertained to be 153°. Seelig therefore concludes that the second or α-dichlorotoluene has the 2 : 3-formula.

Both Wynne and Armstrong throw doubt on this result. Wynne (Trans., 1892, **61**, 1051) regards the evidence in favour of the 2 : 3-formula as inconclusive, and from a comparison of the sodium and barium sulphonates considers the 2 : 5-formula as more probable.

Armstrong (Trans., 1892, **61**, 1035) bases his objection on the analogy offered by the bromination products of toluene studied by Miller, and he also points to the 2 : 5-formula as the more probable. Miller (Trans., 1892, **61**, 1023) states, but on no visible grounds, that by brominating ortho-bromotoluene, 2 : 5-dibromotoluene appeared as the chief and 2 : 4- as a subsidiary product, whilst from para-bromotoluene he obtained 3 : 4- as the chief and 2 : 4- as the subsidiary product.

On the other hand, contrary evidence is afforded by the work of Willgerodt and Salzmann (*J. pr. Chem.*, 1889, [ii], **39**, 465), who showed that by brominating *o*-chlorotoluene the bromine forms the 2 : 4- and 2 : 6-compounds, whilst by chlorinating *p*-bromotoluene, chlorine forms the 2 : 4- and 3 : 4-compounds, no 2 : 5-compound being observed. Since then Claus and Stavenhagen (*Annalen*, 1892, **269**, 224) have found that by chlorinating *o*-chlorotoluene—one of the products of the chlorination of toluene—two dichlorotoluenes are formed, which on oxidation give the 2 : 4- and 2 : 6-dichlorobenzoic acids, from which it appears almost certain that 2 : 6-dichlorotoluene is one of the direct products of chlorination, a fact which is in agreement with the previous observation of Schultz and confirms that of Willgerodt and Salzmann.

If we take the combined results of all these observers, we have more or less clear evidence of the existence of four dichlorotoluenes produced by chlorinating toluene in presence of molybdenum or ferric chloride: 2 : 3-, 2 : 4-, 3 : 4-, 2 : 6-, and a suggestion unsupported by any evidence of a fifth, 2 : 5-dichlorotoluene. No single observer has, however, succeeded in identifying more than three out of the five isomers referred to.

The reason for these conflicting views is readily explained. In chlorinating toluene, a liquid mixture of dichlorotoluenes is formed, from which it is impossible to isolate the different constituents by any process of fractional distillation, seeing that their boiling points lie within a few degrees of each other. The only method which is available is to convert the liquid into a solid derivative, of which the following are most readily prepared: nitro- or dinitro-compound, sulphonic acid, its salts, chloride, amide, or anilide, or the corresponding benzoic acid, and to separate the products by fractional crystallisation. The melting point may then be determined, and the identity of the substance established by comparison with that of a pure product of known constitution. This method may lead to a form of error into which earlier investigators fell. Unless the whole material is investigated from start to finish, some of the products may escape observation. Thus, Beilstein and Kuhlberg carefully fractionated their crude dichlorotoluene until a constant boiling fraction was obtained. No doubt a portion of the products was thus eliminated at the outset. This fraction was oxidised, and the acid which first separated was recrystallised until it had a constant melting point, no other product being sought for in the mother liquor. Thus the acids which were discovered later by Schultz escaped observation.

Seelig has committed errors of a much more serious kind, for he has, apparently, not only omitted to look for compounds obtained by previous observers, but has failed to compare some of his products with the pure substances of known constitution. To quote instances, no attempt was made to isolate the acid (m. p. 128°) obtained by Aronheim, and also by Schultz, and again, the dinitro-compound of m. p. 121° is assumed to be a derivative of the 2 : 3-dichlorotoluene, whereas if he had taken so elementary a precaution as to nitrate pure 2 : 3-dichlorotoluene, he would at once have convinced himself of his error, as this compound melts at 71—72°.

The process of fractional crystallisation is also attended with difficulties, which are emphasised in the case of compounds possessing, like the derivatives of the dichlorotoluenes, not only similar chemical properties, but often nearly identical solubilities in various media. Thus we obtained a nearly constant melting fraction on repeatedly recrystallising some of the dinitro-derivatives, which subsequently proved to be a mixture.

It is only by preparing a variety of derivatives from the liquid mixture that this difficulty may be overcome. A number of opportunities is thereby offered to each isomer of establishing its identity by a distinctive property of one at least of its derivatives.

In pursuing this idea, our research has necessitated the fractional crystallisation of certain of the nitro- and dinitro-derivatives, sulphonic

acids, chlorides, amides, and benzoic acids of the mixed dichlorotoluenes, as well as the preparation of the pure substances for comparison.

The latter are tabulated below, the table also including the results obtained by Wynne (Trans., 1892, 61, 1045).

Melting points of the derivatives of the dichlorotoluenes.

	Nitro.	Dinitro.	Sulphonic chlorides.		Sulphonamides.	
			Wynne.	C. and D.	Wynne.	C. and D.
2 : 3	50·5—51·5°	71—72°	i. 45° ii. 82	—	i. 221° ii. 183	222°
2 : 4	54—55	104	71	71°	177	176
2 : 5	50—51	100—101	43	45—46	191	191—192
2 : 6	53	121—122		—	204	204
3 : 4	63—64	91·5—92·5	82	81	189	190—191
3 : 5	61—62	99—100	45	44—45	168	168—169

We may sum up our results as follows:

Using the aluminium-mercury couple as 'carrier,' we have established the presence of the 2 : 3-, 2 : 4-, 2 : 6-, and 3 : 4-compounds, and the probable existence of small quantities of the 2 : 5-compound. This is in substantial agreement with the products formed with molybdenum or ferric chloride as 'carrier.' In other words, four, and probably five, out of the possible six isomers are produced, the only compound of which we could find no trace being the 3 : 5-isomer. Their presence has been determined from the following evidence.

We have taken as the starting point pure ortho- and para-monochlorotoluene, which were known to form the first products of the chlorination of toluene, which we have confirmed by oxidising the mixture to the benzoic acids and separating the ortho- and para-compounds.

Chlorination of Para-chlorotoluene.

2 : 4-*Dichlorotoluene.*—Evidence of the presence of this compound was obtained by converting the mixture into the dinitro-derivative and fractional crystallisation. The dinitro-compound melting at 103° was isolated, which is identical with that obtained from the pure 2 : 4-dichlorotoluene. On oxidation of the mixed dichlorotoluenes to the corresponding benzoic acids, and by fractional crystallisation of the barium salts, the benzoic acid, m. p. 159°, was obtained, corresponding to the 2 : 4-benzoic acid. Also the sulphonic chloride, m. p. 70°, and the sulphonamide, m. p. 176°, were prepared by sulphonation of the mixed dichlorotoluenes and fractional crystallisation.

3 : 4-*Dichlorotoluene.*—The dinitro-derivative, m. p. 90—92°, was separated from the mother liquors in the fractionation of the above 2 : 4-dinitro-derivative. The corresponding benzoic acid was obtained from the crystallisation of the barium salts described above. It melted at 200—201° in agreement with that of the pure 3 : 4-compound.

Chlorination of Ortho-chlorotoluene.

2 : 3-*Dichlorotoluene.*—The product of chlorination was sulphonated, the barium salt fractionated, and the sulphonamide which was obtained melted at 221°, in agreement with the pure compound. The mixed barium salts were then desulphonated, and the dichlorotoluenes converted into their dinitro-derivatives. By fractional crystallisation, a portion was separated having the m. p. 72°.

2 : 6-*Dichlorotoluene.*—From another fraction of the same mixture of dinitro-compounds, the compound melting at 121—122° was isolated, corresponding to the pure 2 : 6-compound. The crude dichlorotoluene was also oxidised to the corresponding benzoic acid. On treating the mixed acids with methyl alcohol and hydrochloric acid in the cold, some free acid was isolated. According to Victor Meyer's "esterification law," this should be a diortho-substituted acid, and the melting point, 137—139°, corresponds to that of the 2 : 6-dichlorobenzoic acid.

2 : 4-*Dichlorotoluene.*—The portion unsulphonated with concentrated sulphuric acid was treated with fuming sulphuric acid, and the barium salts thus obtained were fractionated. One fraction was converted into the sulphonamide, m. p. 176°, which agrees with that of the pure compound. From the dinitro-derivatives, obtained by nitrating the mixture of chlorinated products, a compound melting at 103° was isolated.

2 : 5-*Dichlorotoluene.*—The only evidence obtained of the presence of this compound was from the crude dichlorotoluene sulphonated with fuming sulphuric acid, from which the previous (2 : 4-) derivative was prepared. This was converted into the sulphonamide and fractionated. The first crop of crystals melted at 189—191°, which corresponds to the 2 : 5-compound. The evidence is admittedly incomplete, and is due to the fact that none of the simple derivatives of the 2 : 5-compound show sufficiently marked characteristics to render them easy to identify.

Chlorination of Meta-chlorotoluene.

To make the series complete, we have included the chlorination of *m*-chlorotoluene within the scope of this research, a subject which has hitherto not been investigated.

2 : 5-*Dichlorotoluene.*—It was identified by the melting point,

100—101°, of the dinitro-compound, which was obtained by fractional crystallisation of the mixture of which it formed a large proportion.

3:4-*Dichlorotoluene.*—This formed the only other constituent, and was identified by oxidising it to the benzoic acid, m. p. 200—201°, and by isolating from the mixed dinitro-compounds a portion melting at 92°. No trace of either the 2 : 3- or the 3 : 5-compounds could be detected. The absence of the 3 : 5-compound would be anticipated from the well-known property of the chlorine atom to enter the ortho- or para- and not the meta-position to the methyl or halogen groups. But the reason for the absence of the 2 : 3-compound is not so apparent, and may be referred to space interference of the meta-groups, which might prevent the introduction of the halogen between them.

The unsatisfactory nature of the research on the bromination of toluene, to which reference has been made (p. 1114), has decided us to repeat this investigation on similar lines to the present one, and we have already made some progress in this direction. We are also completing the investigation of the trichlorotoluenes obtained by the chlorination of the dichlorotoluenes.

Experimental.

For purposes of reference, the experimental part has been divided into the following sections:

	Page
I. Chlorination of benzene	1118
II. „ toluene	1119
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I. *Chlorination of Benzene.*

Monochlorobenzene.—Chlorine washed and dried by concentrated sulphuric acid was passed into benzene contained in a wash-bottle cooled in ice. Fifty grams of benzene, previously distilled over sodium, were introduced into the wash-bottle, together with about 0·5 gram of the aluminium-mercury couple. On passing in the chlorine, the benzene becomes first yellow, then rapidly turns dark violet, and torrents of hydrochloric acid gas are evolved, the couple remaining practically unattacked. When the benzene had increased 13 grams in weight, the process was stopped. The liquid was then washed with caustic soda solution, dehydrated over calcium chloride, and fractionated, with the following result:

Below 127°	4 grams.
127—137	50 „
137—160	5 „
Above 160	4 „

The amount of crude monochlorobenzene corresponds to about 70 per cent. of the theoretical yield.

Para-dichlorobenzene.—From the residue boiling above 160° a solid separated on cooling in ice and salt, which was drained and dried. It was recrystallised from dilute alcohol and melted at 54—56°, which is the melting point of *p*-dichlorobenzene.

Tri- and Tetra-chlorobenzene.—Ten grams of crude chlorobenzene and 10 grams of carbon tetrachloride were introduced into a U-tube with a small piece of the couple and chlorine passed in. The liquid first became yellow, and then a more vigorous action occurred, which was indicated by a rise of temperature and a rapid change of colour to dark brown. This sudden change may possibly correspond to the passage from the additive to the substitution compound, referred to by Seelig in the case of toluene (*Annalen*, 1887, 237, 170). When the requisite amount of chlorine had been absorbed, the current of gas was stopped, and the mixture, to which a little more solvent was added to bring the solid into solution, was shaken with caustic soda, dehydrated, and distilled.

The portion boiling at 130—230°, and amounting to 14 grams, solidified on cooling. It was drained and recrystallised. The greater portion (7 grams) melted at 138°, which corresponds with the 1 : 2 : 4 : 5-compound. About half a gram melted at 127—130°. The oil which was drained off solidified in a freezing mixture, and is probably the 1 : 2 : 4-trichlorobenzene, which melts at 16°.

Hexachlorobenzene.—One gram of the pure tetrachlorobenzene was dissolved in 15 parts of carbon tetrachloride and introduced into a U-tube, with a fragment of the couple and chlorine passed in for some time. A vigorous reaction occurred, heat was evolved, and the liquid became dark violet. The product was washed, and the carbon tetrachloride removed by distillation. The solid residue was washed with ether to remove yellow colouring matter. A theoretical yield (1·4 grams) of hexachlorobenzene was obtained melting at 228—229°.

II. *Chlorination of Toluene.*

Monochlorotoluene.—Chlorine was passed into 62 grams of dry toluene in presence of the couple until an increase of 19·5 grams was obtained. The product was then washed, dried, and fractionated, as follows:

Below 140°	.....	1·5 grams.
140—163	.....	68·7 „
Above 163	.....	2 „

The yield of crude chlorotoluene is about 80 per cent. of the theoretical. The larger portion was distilled with a Hempel column, and the following fractions were obtained:

Below 130°	.....	3·2 grams.
130—150	.....	7 „
150—155	.....	41 „
155—163	.....	17·5 „

With the exception of about a gram, the large fraction boiled constantly at 154—155°, and is therefore mainly *o*-chlorotoluene, b. p. 154°.

The para-compound, according to different observers, boils at 160° and 163°. In order to identify the ortho-compound, it was oxidised to chlorobenzoic acid. Five grams of the chlorotoluene, 16 grams of potassium permanganate, and 210 c.c. of water were boiled together for 7 hours with a reflux condenser. Sulphur dioxide was then passed into the liquid to dissolve the manganese dioxide and precipitate the acid. The chlorobenzoic acid was then boiled with water, which left 0·7 gram undissolved. This residue melted at 235°, and was therefore *p*-chlorobenzoic acid (m. p. 236°). The solution deposited 2·8 grams of crystals which, after recrystallisation, melted at 134—135°, corresponding to the melting point of the *o*-chlorobenzoic acid. The same process was repeated with a fraction boiling at 157—163°. This was much less readily oxidised, but eventually from 5 grams 2·65 grams of mixed acids were obtained, which were separated by hot water, and gave 0·9 gram of the ortho-compound melting at 132—134°, the remainder being the para-compound melting at 233—234°. The mixture of crude monochlorotoluenes consists therefore of, approximately, 65 per cent. of ortho- and 35 per cent. of para-compound. This agrees with Seelig's results (*loc. cit.*).

Dichlorotoluene.—Sixty grams of toluene were chlorinated as before until the increase in weight amounted to 36 grams. The liquid was purified and fractionated, as follows:

110—145°	.....	18·5 grams.
145—180	.....	7·5 „
180—210	.....	65 „
Above 210	.....	2 „

The portion boiling below 180° was again chlorinated and distilled. It gave:

Below 180°	.....	12 grams.
180—210	.....	12 „

Thus 77 grams of crude dichlorotoluene were obtained from 60 grams of toluene, corresponding to 74 per cent. of the theoretical yield. The 77 grams were refractionated.

160—194°	22 grams.
194—200	50 „
Above 200	5 „

The 22 grams, b. p. 160—194°, were subsequently re-chlorinated for the preparation of trichlorotoluene.

An attempt was made to identify the dichlorotoluenes by oxidation to the corresponding acids with potassium permanganate, but the process gave a very unsatisfactory result and was abandoned. From 30 grams of crude dichlorotoluene, after boiling with 80 grams of permanganate and 1200 c.c. of water for 7 days in a calcium chloride bath, only 3 grams of acid were obtained melting at 157—164°. A slight modification of this method, which was recommended by Claus and Stavenhagen (*Annalen*, 1892, **269**, 24), has not in any way helped to convince us of its efficacy (see p. 1132).

Trichlorotoluene.—The 22 grams of liquid boiling at 160—194°, obtained as above described in the preparation of dichlorotoluene, were further chlorinated until there was an increase of 4·5 grams in weight. After the usual purification, the liquid was fractionated as follows:

Below 220°	4 grams.
220—240	17 „
240—262	13 „

The last two fractions solidified on cooling. Both portions were separately recrystallised from alcohol, and the two principal fractions which were obtained melted at 82° and 40—42°. This agrees exactly with Seelig's melting points of the two trichlorotoluenes which he isolated. At least two trichlorotoluenes are therefore present.

III. *Dichlorotoluene and its Derivatives from Para-chlorotoluene.*

Sixty-one grams of *p*-chlorotoluene (b. p. 156—160°), prepared by Gattermann's method from *p*-toluidine, were treated with chlorine in presence of the couple, until an increase of 20 grams was obtained. The product was purified and distilled.

Below 190°	1·5 grams.
190—210	59·5 „
210—230	13·5 „
Above 230	2 „

The two intermediate fractions were redistilled.

190—197°	22 grams.
197—205	30 „

Nitration of the Mixed Dichlorotoluenes.

Each of the above two fractions was nitrated as follows.

Five grams of the dichlorotoluene were added in small quantities to a cooled mixture of 17 grams of concentrated sulphuric acid and 34 grams of fuming nitric acid (sp. gr. 1·5). The mixture was kept cool until all the dichlorotoluene had been added. It was then warmed on the water-bath for about 15 minutes and poured on to crushed ice. The solid was filtered, washed with water, and dried on a porous plate.

The substance was fractionally crystallised from alcohol and from glacial acetic acid. Five grams of dichlorotoluene, boiling at 190—197°, gave 5·4 grams of a dinitro-compound, of which 3·7 grams melted at 102—103°, corresponding to the 2 : 4-compound. The remainder melted indefinitely at about 80°, but by prolonged fractionation a small quantity of fine needles was obtained melting at 90—92°, which corresponds to the 3 : 4-derivative. Six grams of the fraction boiling at 197—205° gave 7·7 grams of dinitro-compound, of which 4·1 grams melted at 101—103°. The remainder melted at a lower temperature, and was probably a mixture of the 2 : 4- and 3 : 4-derivatives, as in the previous fraction.

Oxidation of the Mixed Dichlorotoluenes.

Five grams of the dichlorotoluene were heated for 6 hours at 140° in a sealed tube with a mixture of 13 c.c. of concentrated nitric acid (sp. gr. 1·4) and 15 c.c. of water. The product was made alkaline with caustic soda, and a trace of unoxidised substance removed by steam distillation. The mixed dichlorobenzoic acids were then precipitated by the addition of hydrochloric acid. After filtration and washing, the benzoic acids were converted into their barium salts by boiling the aqueous solution with a slight excess of baryta. The salts were repeatedly crystallised from hot water. The most insoluble barium salt, after three crystallisations, yielded a dichlorobenzoic acid melting at about 190°. The acid was then recrystallised four times from dilute spirit, when it melted sharply at 200°, corresponding to the 3 : 4-dichlorobenzoic acid.

The more soluble barium salt yielded an acid melting at about 150°. On repeatedly crystallising, a pure product was isolated melting at 159°, corresponding to the 2 : 4-dichlorobenzoic acid.

Sulphonation of the Mixed Dichlorotoluenes.

Five grams of the dichlorotoluene mixture were sulphonated with fuming sulphuric acid and the sodium salt separated by pouring into brine. This was converted into the sulphonic chloride with phosphorus pentachloride. On fractional crystallisation of the sulphonic chloride from petroleum, a product melting at 70° was obtained, corresponding to the 2 : 4-derivative. The sulphonamide was then prepared, which, on fractional crystallisation, indicated the presence of two compounds, only one of which, the 2 : 4-sulphonamide melting at 176°, could be prepared in the pure state.

Dichlorotoluene and its Derivatives from Ortho-chlorotoluene.

o-Chlorotoluene was obtained from *o*-toluidine by Wynne's modification of Sandmeyer's method (Trans., 1892, **61**, 1072). Fifty-four grams of the product boiling at 154—158° were chlorinated as previously described, and the following fractions obtained:

Below 190°	.....	3·5 grams.
190—210	.....	51 „
210—230	.....	7 „
Above 230	.....	3 „

The fraction boiling at 190—210° was then redistilled.

190—195°	.....	7 grams.
195—208	.....	42 „

Nitration of the Mixed Dichlorotoluenes.

Five grams of dichlorotoluene were nitrated as previously described and the product fractionated. 0·95 gram of a pure substance melting at 102° was isolated, which corresponds to the 2 : 4-derivative, and a large quantity of a mixture of the nitro-compounds, from which no pure product could be separated. This method of attacking the problem was therefore abandoned.

Sulphonation of the Mixed Dichlorotoluenes.

In order to obtain direct evidence of the existence of the different dichlorotoluenes in the mixture, the product was sulphonated, and the sulphonic acids separated and converted into the sulphonamides. Eighty grams of dichlorotoluene, boiling at 195—208°, were heated on the water-bath with four times the weight of concentrated sulphuric acid, and stirred continuously with a mechanical

stirrer. The mixture was then diluted with water, and unchanged oil removed by distillation in steam. The sulphonic acid was converted into the soluble barium salt by the addition of barium carbonate, and the liquid filtered. The residue was boiled up repeatedly with fresh quantities of water and the united filtrates evaporated. In this way, 36 grams (fraction 1) of the barium salt crystallised out, and a further 7 grams (fraction 2) were obtained by evaporation of the mother liquor. The recovered portion, which had not been sulphonated, amounted to 58 grams, and was treated with 160 grams of 20 per cent. fuming sulphuric acid. The dichlorotoluene, on shaking, rapidly dissolved. It was diluted and distilled in steam, and 10·5 grams of unchanged dichlorotoluene were recovered. Fraction 1 gave a sulphonamide which softened at 204° and melted at 210—212°. After five recrystallisations from alcohol, a pure product melting at 221—221½° was obtained. The sulphonamide which was mixed with it was subsequently shown to be the 2 : 6-derivative melting at 204°.

The remainder of the barium salt from fraction 1 was then desulphonated by Armstrong and Miller's method (Trans., 1884, 45, 148). Twenty-two grams of the barium salt, 8 c.c. of water, and 100 grams of concentrated sulphuric acid gave 8 grams of dichlorotoluene boiling at 195—196°. This dichlorotoluene was converted into the dinitro-compound in the ordinary way, and by careful fractional crystallisation from glacial acetic acid the following pure compounds were obtained. (i) A dinitro-compound melting at 120—121° corresponding to the 2 : 6-derivative; (ii) a compound melting at 71—72°, corresponding to the 2 : 3-derivative; (iii) a very small quantity of prisms melting at 103°, identified as the 2 : 4-compound.

The second small fraction of the barium salt gave a sulphonamide which melted indefinitely at about 180°. No pure product was separated from it. It was probably mainly the 2 : 4-derivative.

The third crop of barium salt was converted into the sulphonamide, which was then fractionally crystallised from alcohol. Two compounds were isolated, one melting at 176°, which was identified as the 2 : 4-derivative, the other melting at 189—191°, which was possibly the 2 : 5-derivative. The melting point was unchanged by recrystallisation.

Oxidation of the Mixed Dichlorotoluenes.

Five grams of the dichlorotoluene mixture were oxidised by heating for 6 hours to 130° in a sealed tube with 10 c.c. of nitric acid (sp. gr. 1·4) and 20 c.c. of water. The dichlorobenzoic acids were separated and purified as previously described, (p. 1122). Five grams of the acids were dissolved in 50 c.c. of methyl alcohol, and

dry hydrochloric acid passed into the cold liquid to saturation. The liquid, after standing several hours, was poured into water, and the unchanged dichlorobenzoic acid and esters extracted with ether. The ethereal solution was then repeatedly extracted with small quantities of caustic soda solution, and the alkaline liquid, after boiling off any residual ether, was acidified with hydrochloric acid. The precipitated dichlorobenzoic acid contained some oily impurity, possibly nitro-compounds, which were removed as far as possible by careful draining and pressing on a porous plate. The residual acid was then crystallised from water, 0·65 gram of acid being obtained, which melted indefinitely at 120—134°. The acid was then treated with methyl alcohol and hydrochloric acid as before, and after recrystallisation from dilute spirit, melted at 137—139°. This corresponds to the melting point of the 2 : 6-dichlorobenzoic acid given by Wynne and Greeves (Proc., 1895, **11**, 151. See also p. 1131) and obtained by ourselves.

Dichlorotoluene and its Derivatives from Meta-chlorotoluene.

m-Chlorotoluene was prepared from *m*-toluidine by Sandmeyer's reaction, using cold cuprous chloride solution. The yield from 75 grams of the base amounted to 62 grams of the pure compound boiling at 158—161°. The chlorination was carried out in exactly the same way as previously described, the yield of the mixed dichlorotoluenes amounting to about 85 per cent. of the theoretical amount.

The details of one experiment are as follows. Thirty grams of *m*-chlorotoluene were chlorinated in presence of the couple until the theoretical amount of chlorine had been absorbed. Caustic soda was then added and the product distilled in steam. The distillate was then separated, dried, and fractionated.

Below 195°	1 gram.
195—201	33 „
Above 201	1·5 „

The constituents of the dichlorotoluene thus obtained were identified by means of their dinitro-derivatives and sulphonamides, and also by oxidation to the corresponding benzoic acids.

Nitration of the Mixed Dichlorotoluenes.

The dichlorotoluene mixture was nitrated in the ordinary way, and the dinitro-derivative separated and crystallised from acetic acid. The product melted indefinitely at 86—93°, indicating the presence of a mixture. It was then submitted to systematic fractional crystallisa-

tion, using acetic acid as solvent. The main product was found to consist of a dinitro-compound melting at 99—100°, identical with that obtained from 2 : 5-dichlorotoluene (m. p. 100—101°). From the mother liquors, a product was obtained melting indefinitely at 70—85°. On fractionating this further, a pure substance was separated melting at 92—93°, which is the same as that obtained from 3 : 4-dichlorotoluene melting at 91·5—92·5°. No other compounds having definite melting points were isolated.

Oxidation of the Mixed Dichlorotoluenes.

The oxidation was effected by heating the dichlorotoluene mixture with 7 parts by weight of dilute nitric acid in a sealed tube to 140° for 5 hours. The contents of the tube were dissolved in caustic soda, and the solution distilled in steam to remove a trace of unoxidised substance. The benzoic acids were then precipitated with hydrochloric acid. An unsuccessful attempt was made to separate the constituents of the mixture by fractional distillation in steam. The acids were therefore converted into the barium salts, which were fractionally crystallised. The most insoluble fraction yielded an acid melting at 180—195°, which, on recrystallisation from spirit, melted at 199—200°, and therefore corresponds to the 3 : 4-compound.

The more soluble barium salt yielded a large quantity of an acid which, after repeated crystallisation, melted at 146—148°. This acid probably consists mainly of the 2 : 5-compound (m. p. 153°), but the pure acid could not be obtained.

Sulphonation of the Mixed Dichlorotoluenes.

The sulphonation was undertaken with the special object of detecting the presence of any of the 2 : 3-derivative, as it yields a characteristic sulphonamide. An unsuccessful attempt was made to effect a partial separation of the mixture by using different strengths of sulphuric acid for the sulphonation. As ordinary sulphuric acid had little action, the sulphonation was effected by means of slightly fuming acid, and the product converted into the barium salt. The salt was fractionally crystallised from water, and then the fractions converted into the sulphonamides.

No indication was obtained of the 2 : 3-sulphonamide. The sulphonamides of the 3 : 4- and 2 : 5-compounds previously shown to be present melt too closely together to admit of separation, namely, 3 : 4- at 190—191° and 2 : 5- at 191—192°. No 3 : 5-dichlorotoluene could be detected in any of the reactions.

The conclusion is therefore drawn that of the four possible dichloro-

toluenes theoretically obtainable from *m*-chlorotoluene, only the 2 : 5- and 3 : 4-compounds are formed, the former being present in the larger quantity.

IV. *Preparation of the Six Dichlorotoluenes and their Derivatives. Preparation of* 2 : 3-*Dichlorotoluene.*

3-*Nitro*-2-*toluidine.*—2 : 3-Dichlorotoluene was prepared from the corresponding nitrotoluidine. Lellmann and Würthner (*Annalen*, 1885, 228, 239) found that *o*-acetotoluidide gave on nitration two nitro-acetotoluidides, which were separated by means of fractional hydrolysis, followed by mechanical sieving of the mixed crystalline product. The two compounds were identified as the 2 : 3- and 2 : 5-nitro-derivatives. Reverdin and Crépieux (*Ber.*, 1900, 33, 2498) have described a more convenient method of separating the two isomers. They find that if the mixed product of nitration be hydrolysed with concentrated hydrochloric acid and the acid liquid distilled in steam, the 2 : 3-compound is volatilised, whilst the 2 : 5-compound remains behind. From the results of a number of experiments, we find that the best results are obtained as follows.

Fifteen grams of powdered *o*-acetotoluidide are added in small portions to a mixture of 50 grams of fuming nitric acid and 18 grams of glacial acetic acid, the temperature being maintained at about 15°. If the liquid is cooled below this temperature, the reaction is suspended for a time until all the acetotoluidide has been added, when it sets in vigorously with rapid rise of temperature and ultimate decomposition. After standing some hours at the ordinary temperature, water is added to the solution, and the precipitated nitro-compounds filtered off and washed. The substance is then placed in a flask with the addition of 40 c.c. of concentrated hydrochloric acid and, without any preliminary heating, distilled in steam. After a short time, orange coloured crystals collect in the receiver, distillation being continued until no more solid matter is carried over, an operation which lasts about 6 hours. The yield amounts to 6—7 grams of 2 : 3-nitrotoluidine. The 2 : 5-compound may be separated from the acid liquid remaining in the distilling flask.

2-*Chloro*-3-*nitrotoluene.*—Three parts of finely powdered nitrotoluidine were suspended in 5 parts of concentrated hydrochloric acid and 4 parts of water, and the cooled liquid diazotised by the addition of solid sodium nitrite.

In this and in subsequent preparations we found the solid nitrite in coarse pieces to act more slowly and effectively and with a much smaller rise of temperature than the nitrite solution. When the base had gone into solution, the liquid was added to an ice-cold solution of

4 parts of cuprous chloride dissolved in concentrated hydrochloric acid as described by Wynne (Trans., 1892, **61**, 1072).

When the evolution of nitrogen had ceased, the liquid was distilled in steam. An almost theoretical yield of chloronitrotoluene was obtained.

2-*Chloro*-3-*toluidine*.—The above nitro-compound was reduced by means of a slight excess of stannous chloride dissolved in an equal weight of concentrated hydrochloric acid. The reaction, which was at first very vigorous, was completed by heating for an hour on the water-bath. At the end of this time, a clear solution was obtained which was poured into a basin and left to crystallise. The crystalline mass was pressed on the filter, and washed with a little concentrated hydrochloric acid. A small quantity of tin was removed from the crystals by dissolving them in hot water and passing in sulphuretted hydrogen. The sulphide was removed by filtration, the filtrate concentrated, and the crystalline hydrochloride used in the subsequent process.

2 : 3-*Dichlorotoluene*.—The conversion of chlorotoluidine into di chlorotoluene is carried out in the same manner as in the preparation of chloronitrotoluene from nitrotoluidine. The yield was nearly theoretical. On fractional distillation, 90 per cent. boiled at 204—206° at 755 mm. pressure.

2 : 3-*Dichlorobenzoic acid*.—One part of dichlorotoluene was heated with 6 parts of dilute nitric acid (2·5 vols. of concentrated nitric acid sp. gr. 1·4, 3 vols. of water) for some hours in a sealed tube to 140°. The contents of the tube were made alkaline with caustic soda and distilled in steam to remove unchanged dichlorotoluene. The chlorobenzoic acid was precipitated in the residue on the addition of acid and recrystallised from hot water. It melted at 163°.

Nitro-2 : 3-*dichlorotoluene*.—This compound was prepared by adding to 1 part of dichlorotoluene a cold mixture of 2 parts of nitric acid (sp. gr. 1·4) and 3 parts of concentrated sulphuric acid. The mixture was then heated for some time on the water-bath, and the nitro-compound precipitated by pouring on to crushed ice. It was recrystallised from a mixture of alcohol and acetic acid, and was obtained in the form of felted masses of fine needles melting sharply at 50·5—51·5°.

0·1640 gave 0·2292 AgCl. Cl = 34·55.

$C_7H_5Cl_2 \cdot NO_2$ requires Cl = 34·41 per cent.

Dinitro-2 : 3-*dichlorotoluene*.—The dinitro-derivative was obtained by slowly adding to 1 part of dichlorotoluene 7 parts of fuming nitric acid (sp. gr. 1·5) and 3½ parts of concentrated sulphuric acid. The reaction was completed by heating for some time on the water-bath, and the product then poured into water. The precipitated dinitro-

compound was filtered, washed and dried, and recrystallised from glacial acetic acid or alcohol. The product was fractionally crystallised and proved to be uniform. It melted at 71—72°.

0·1991 gave 0·2285 AgCl. Cl = 28·32.

$C_7H_4Cl_2(NO_2)_2$ requires Cl = 28·12 per cent.

2 : 3-*Dichlorotoluenesulphonamide.*—The dichlorotoluene was sulphonated by heating for a short time with three times the weight of fuming sulphuric acid, and the sulphonic acid converted into the barium salt in the usual way. The barium salt was then heated with an equal weight of phosphorus pentachloride, which yielded the sulphonic chloride, and this was converted into the amide in the usual way. The sulphonamide, after recrystallisation from alcohol, melted at 222°.

2 : 3-Dichlorotoluene has been stated by Wynne (Proc., 1895, **11**, 151) to yield two sulphonic acids on sulphonation, which may be separated by fractional crystallisation of their barium salts. Experiments made with the object of separating the two acids failed to indicate the presence of a second acid.

Preparation of 2 : 4-*Dichlorotoluene.*

Ordinary dinitrotoluene was used for the preparation according to the method of Lellmann and Klotz (*Annalen*, 1885, **231**, 308). The dinitrotoluene was first reduced to nitrotoluidine with ammonium sulphide. The product (m. p. 76°) was then submitted to the same series of reactions as previously described under 2 : 3-dichlorotoluene. The yields throughout were satisfactory. Fifty grams of dinitrotoluene yielded 18 grams of 2 : 4-dichlorotoluene boiling at 198—200°.

2 : 4-*Dichlorobenzoic Acid.*—This acid was obtained by oxidising the dichlorotoluene with dilute nitric acid in a sealed tube at 130—140°. The product was purified in the usual way, and crystallised from hot water in fine needles melting at 159—160°.

Nitro-2 : 4-*dichlorotoluene.*—This compound was prepared in the same way as the 2 : 3-compound, and crystallised from spirit in long, hard needles melting at 54—55°. Seelig gives 53° as the melting point of this substance.

Dinitro-2 : 4-*dichlorotoluene* was prepared in the manner described under the 2 : 3-compound. It crystallised from a mixture of glacial acetic acid and alcohol in fine prisms melting at 104° (Seelig gives 102°).

2 : 4-*Dichlorotoluenesulphonamide.*—2 : 4-Dichlorotoluene is readily sulphonated with fuming sulphuric acid. The sodium salt was separated by pouring the product into brine, which was then converted

into the sulphonic chloride. The latter crystallised from petroleum ether in hard prisms melting at 71°. The sulphonamide was repeatedly crystallised from spirit and melted sharply at 176°.

Preparation of 2 : 5-*Dichlorotoluene.*

The 2 : 5-dichlorotoluene was obtained in two ways, (i) by direct chlorination of *o*-acetotoluidide (Lellmann and Klotz, *Annalen*, 1885, 231, 319), and (ii) by the action of sodium hypochlorite on *o*-acetotoluidide (Chattaway and Orton, Trans., 1900, 77, 790). The two products were identical.

(i) Following Lellmann and Klotz's directions, *o*-acetotoluidide was dissolved in sufficient glacial acetic acid to prevent crystallisation on cooling, and a current of dry chlorine passed into the cooled liquid. A vigorous reaction occurs with considerable rise in temperature. After a time, the solution suddenly becomes almost solid. Water was then added, and the crude chloroacetotoluidide filtered off and recrystallised from spirit. On hydrolysis with concentrated hydrochloric acid, the hydrochloride of chlorotoluidine separated in the form of crystals with a satin-like lustre. The amino-group was replaced by chlorine by Wynne's modification of Sandmeyer's method already referred to. From 45 grams of *o*-acetotoluidide, 22 grams of crude dichlorotoluene were obtained, of which 19 grams boiled constantly at 198—199° under a pressure of 760 mm. The product solidified completely in a freezing mixture, and melted sharply at 5°.

(ii) Twenty grams of *o*-acetotoluidide were shaken up with 400 c.c. *N*/2 sodium hypochlorite solution containing 20 grams of sodium bicarbonate and left to stand 24 hours. A little chloroform was added and the lower layer of liquid withdrawn. About an equal volume of glacial acetic acid and a drop of concentrated sulphuric acid were then added to the chloroform solution, which was warmed on the water-bath. The greater part of the chloroform evaporated, and the chloroacetotoluidide was precipitated by pouring into water. The yield was nearly theoretical. The crude product was recrystallised from dilute spirit and hydrolysed by boiling with excess of concentrated hydrochloric acid. The subsequent operations were identical with those described under the first method. Twenty-four grams of the chlorotoluidine hydrochloride yielded 15 grams of pure dichlorotoluene boiling at 198—200° at 760 mm. and melting at 5°.

2 : 5-*Dichlorobenzoic acid* was obtained by oxidation with dilute nitric acid at 140°. The product was recrystallised three times from dilute spirit, and melted sharply at 153°.

Nitro-2 : 5-*dichlorotoluene.*—Great care was required in this preparation to prevent the formation of the dinitro-derivative. The following

proportions gave satisfactory results. A cold mixture of $1\frac{1}{2}$ parts of concentrated nitric acid (sp. gr. 1·4) and 3 parts of concentrated sulphuric acid were slowly added to 1 part of the dichlorotoluene, any great rise of temperature being avoided. The mixture was subsequently warmed on the water-bath and the nitro-compound precipitated by water. On recrystallisation from a mixture of alcohol and ether, the nitro-compound was obtained in the form of fine needles melting at 50—51°.

0·1192 gave 0·1655 AgCl. Cl = 34·33.

$C_7H_5Cl_2 \cdot NO_2$ requires Cl = 34·41 per cent.

Dinitro-2 : 5-*dichlorotoluene* was prepared by the method already described in the case of the other dinitro-compounds. It was recrystallised from glacial acetic acid and melted at 100—101°.

0·2630 gave 0·3015 AgCl. Cl = 28·33.

$C_7H_4Cl_2N_2O_4$ requires Cl = 28·12 per cent.

2 : 5-*Dichlorotoluenesulphonamide.*—The dichlorotoluene was sulphonated with fuming sulphuric acid, and the product separated as the sodium salt. The sulphonic chloride prepared by the action of phosphorus chloride on the sodium salt crystallised from ether in large, colourless plates melting at 45—46°. The sulphonamide was obtained in the form of colourless needles melting at 191—192°.

Preparation of 2 : 6-*Dichlorotoluene.*

The 2 : 6-nitrotoluidine, which served as the starting point for the preparation of the dichlorotoluene, we owe to the great kindness of Messrs. Green and Lawson, who obtained it in small quanties as a by-product by nitrating *o*-toluidine (Trans., 1891, **59**, 1013). An almost theoretical yield of chloronitrotoluene was obtained in the form of fine, yellow crystals by using Wynne's modification of Sandmeyer's reaction. The reduction of the nitro-compound was effected with stannous chloride, when the hydrochloride of chlorotoluidine was obtained in the form of white, glistening plates. From the latter, the 2 : 6-dichlorotoluene was finally prepared. Ten grams of the nitrotoluidine yielded 4·5 grams of pure dichlorotoluene, boiling constantly at 198° at a pressure of 760 mm.

2 : 6-*Dichlorobenzoic acid* was obtained by oxidation in a sealed tube with nitric acid. After frequent recrystallisation, the product melted at 132—133°, which agrees with the number given by Claus and Stavenhagen (*Annalen*, 1892, **269**, 224), but is much lower than that given by Wynne and Greeves (139°) or previously obtained by us from the mixture of dichlorotoluenes prepared by chlorinating *o*-chlorotoluene (see p. 1125). We concluded, therefore, that both Claus' and our pro-

ducts were impure. In our case, the fact was easily explained, for 2 : 6-dichlorotoluene is very difficult to oxidise. Heated with very dilute nitric acid in a sealed tube, it is only slightly attacked, whereas with stronger acid nitro-compounds are formed which lower the melting point of the product. On the other hand, Claus and Stavenhagen's method (*loc. cit.*) of preparing 2 : 6-dichlorobenzoic acid from the crude chlorination product of *o*-chlorotoluene by oxidising with powdered potassium permanganate absolutely failed in our hands. Although we followed in detail the directions given, we found, after 2 days' boiling, that only a trace of dichlorotoluene had been attacked. We conclude that some important omission must have been made in the description of the method. We ultimately used the following method, which gave a satisfactory result.

Five grams of the dichlorotoluene were oxidised with 10 c.c. of concentrated nitric acid (sp. gr. 1·4) and 20 c.c. of water for a day at 140° in a sealed tube. Caustic soda was added to the product, and the liquid distilled in steam. A small amount of solid distilled, which was identified as 2 : 6-dichlorobenzaldehyde. On acidifying the alkaline solution, an acid was obtained melting at 128—132°. The impure acid was treated with a solution of 5 grams of stannous chloride in 10 c.c. of concentrated hydrochloric acid, and heated for an hour on the water-bath. The acid liquid was then extracted with ether, from which the dichlorobenzoic acid was obtained by washing with caustic soda solution. The acid was precipitated by the addition of hydrochloric acid. It was further purified by dissolving in methyl alcohol, saturating with dry hydrochloric acid, and allowing it to stand for a time. On pouring into water and extracting with ether, the acid went into solution in the ether, from which it was extracted with caustic soda solution. On acidifying the alkaline solution, the acid was precipitated, and, after crystallisation from water, formed colourless needles melting at 139—140°.

Nitro-2 : 6-*dichlorotoluene* was obtained in the usual way and crystallised from a mixture of alcohol and acetic acid in needles melting sharply at 53°.

0·1222 gave 0·1720 AgCl. Cl = 34·79.

$C_7H_5Cl_2 \cdot NO_2$ requires Cl = 34·41 per cent.

Dinitro-2 : 6-*dichlorotoluene* was prepared by the method previously described. It crystallised from alcohol in flattened needles melting at 121—122°.

0·0695 gave 0·0792 AgCl. Cl = 28·17.

$C_7H_4Cl_2(NO_2)_2$ requires Cl = 28·12 per cent.

2 : 6-*Dichlorotoluenesulphonamide*.—The dichlorotoluene was readily

sulphonated with fuming sulphuric acid, the product being separated as the sodium salt. The latter was converted into the sulphonic chloride and sulphonamide. The sulphonamide was crystallised from alcohol and melted at 204°.

Preparation of 3 : 4-*Dichlorotoluene.*

The starting point for this preparation was the 3 : 4-nitrotoluidine supplied by Kahlbaum in beautiful, large, red crystals. The various steps in the process are the same as described in the case of the other nitrotoluidines and call for no special remark. Fifty grams of the nitrotoluidine yielded 17 grams of pure dichlorotoluene boiling at 200—207°.

3 : 4-*Dichlorobenzoic acid* was obtained by oxidising with dilute nitric acid at 130—140°. The acid, which is slightly volatile in steam, melted at 200—201°.

Nitro-3 : 4-*dichlorotoluene.*—Care is required to prevent the formation of the dinitro-derivative. The best results were obtained by using 2 parts of concentrated nitric acid (sp. gr. 1·4) and 4 parts of concentrated sulphuric acid to 1 part of dichlorotoluene. The product crystallises from alcohol and acetic acid in fine, long needles melting at 63—64°.

0·1000 gave 0·1395 AgCl. Cl = 34·48.

$C_7H_5Cl_2 \cdot NO_2$ requires Cl = 34·41 per cent.

Dinitro 3 : 4-*dichlorotoluene* was easily obtained, and crystallises from glacial acetic acid in long, nearly colourless needles melting at 91·5—92·5°.

0·2557 gave 0·2920 AgCl. Cl = 28·23.

$C_7H_4Cl_2N_2O_4$ requires Cl = 28·12 per cent.

3 : 4-*Dichlorotoluenesulphonamide.*—The dichlorotoluene was readily sulphonated and converted into the sodium salt. The sulphonic chloride solidifies readily and crystallises from ether in long needles melting at 81°. The sulphonamide melts at 190—191°.

Preparation of 3 : 5-*Dichlorotoluene.*

The method employed for the preparation of the 3 : 5-dichlorotoluene is that described by Chattaway and Orton (Trans., 1900, 77, 791).

Thirty grams of *o*-acetotoluidide were dissolved in 120 c.c. of glacial acetic acid, and a solution of 100 grams of bleaching powder in 2 litres of water were added. After standing 12 hours, the supernatant liquid was decanted from the yellow oil. To the latter, about an equal volume of glacial acetic acid and a few drops of concentrated sulphuric

acid were added, and the solution was then warmed on the water-bath. After standing for a time, the solution was poured into water, when the dichloroacetotoluidide separated out. It was filtered, washed, and crystallised from spirit. The yield is nearly theoretical. The hydrolysis was effected by heating 1 part of the dichloro-compound with 3 parts of concentrated hydrochloric acid to 150° in a sealed tube for 8 hours. In this way, 21 grams of the dichlorotoluidine were obtained from 30 grams of the dichloroacetotoluidide. By using Claus' method, on the other hand, alcoholic potash only hydrolysed one-half of the compound after two days' boiling. This slow hydrolysing action of potash may be accounted for by space interference, as the amino-group is protected by two ortho-positions. The amino-group in dichlorotoluidine was eliminated by the method of Chattaway and Evans (Trans., 1896, **69**, 850).

Eleven grams of dichlorotoluene were obtained from 21 grams of the base. It possessed the melting point 26° which is that given by Lellmann and Klotz (*Annalen*, 1885, **231**, 320).

3 : 5-*Dichlorobenzoic acid* was obtained by oxidation with dilute nitric acid at 150°. After repeated crystallisation, the compound was obtained in the form of fine, long needles melting at 182—183°.

Nitro-3 : 5-*dichlorotoluene* crystallises from a mixture of alcohol and acetic acid in needles melting at 61—62°.

0·1306 gave 0·1820 AgCl. Cl = 34·45.

$C_7H_5Cl_2{\cdot}NO_2$ requires Cl = 34·41 per cent.

Dinitro-3 : 5-*dichlorotoluene*.—The first preparations of this compound contained the trinitro-derivative, which is readily formed and crystallises in lustrous leaflets melting at about 190°. The pure dinitro-compound was obtained by using the following quantities of materials. Four parts of nitric acid (sp. gr. 1·5) and 4 parts of concentrated sulphuric acid were added to 1 part of the dichlorotoluene. The product crystallises from alcohol in long, white needles melting at 99—100°.

0·1212 gave 0·1390 AgCl. Cl = 28·35.

$C_7H_4Cl_2N_2O_4$ requires Cl = 28·12 per cent.

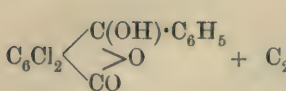
3 : 5-*Dichlorotoluenesulphonamide*.—Sulphonation was readily effected in the ordinary way and the sulphonate converted into the sulphonic chloride, which crystallised from petroleum in large, thick prisms melting at 44—45°. The sulphonamide crystallised from spirit in needles melting at 168—169°.

CXXI.—*The Esterification of 3-Nitrophthalic Acid.*

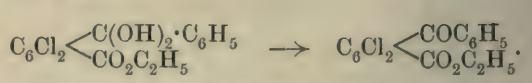
By Alex. McKenzie, Grocers' Company Research Scholar.

Victor Meyer's rule for the ester formation of aromatic acids is of such general applicability that exceptions to it present certain points of interest. Such an exception is 3-nitrophthalic acid. Faust (*Annalen*, 1871, **160**, 56) obtained a crystalline ethyl hydrogen ester by conducting the esterification in the cold, whilst a normal ester resulted as an oil on rise of temperature. Since, however, the product of the nitration of phthalic acid has been shown by O. Miller to be a mixture of 3- and 4-nitrophthalic acids, and is not homogeneous as Faust apparently supposed, much weight could not be attached to the observation of the latter investigator. The different behaviour of the isomeric nitrophthalic acids on esterification by the hydrogen chloride method was noted by Miller (*Ber.*, 1878, **11**, 1191; *Annalen*, 1881, **208**, 227), who points out that when the mixture resulting from the nitration of phthalic acid is directly esterified, the 4-nitrophthalic acid is converted into the normal ester, the 3-nitrophthalic acid, on the other hand, slightly into the normal ester, and mainly into the acid ester. V. Meyer and Sudborough (*Ber.*, 1894, **27**, 3151) suggested that the presence of this normal ester might possibly be attributed to the prolonged action of the methyl alcohol and mineral acid causing slight decomposition of the 3-nitrophthalic acid into mononitrobenzoic acid, the melting point of the methyl ester of which agrees closely with that observed by Miller for the normal ester. Wegscheider and Lipschitz (*Monatsh.*, 1900, **21**, 787) have supplied experimental evidence for the invalidity of this hypothesis by hydrolysing the normal methyl ester produced on the esterification of 3-nitrophthalic acid by the sulphuric acid method, and by identifying the resulting compound as 3-nitrophthalic acid.

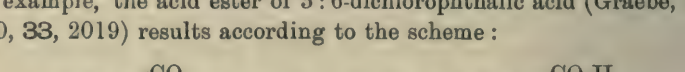
With regard to the explanations adduced to account for the deviations from the V. Meyer rule, Graebe's observation that tetrachlorophthalic acid formed an ethyl hydrogen ester when esterified by the hydrogen chloride method (*Annalen*, 1887, **238**, 327), was attributed by V. Meyer and Sudborough (*loc. cit.*) to the probable existence of tautomeric forms, the acid esters of substituted phthalic acids being represented, for instance, as $C_6H_4<\begin{matrix}CO_2R\\CO_2H\end{matrix}$ and $C_6H_4<\begin{matrix}RO\quad OH\\C\\CO\end{matrix}>O$. Similarly, Graebe (*Ber.*, 1900, **33**, 2027) supposes that in the esterification of 3 : 6-dichlorobenzoylbenzoic acid, which is also an exception to the V. Meyer rule, the acid acts as the tautomeric oxyphthalide, thus:



$$+ \ C_2H_5\cdot OH \ =$$



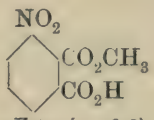
V. Meyer, as well as Wegscheider, assumes that the anhydride is the intermediate product, and that this is further acted on by the alcohol; for example, the acid ester of 3 : 6-dichlorophthalic acid (Graebe, *Ber.*, 1900, **33**, 2019) results according to the scheme:



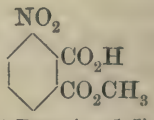
and, when attempts are made to convert it into the normal ester, its comportment accords with the V. Meyer rule.

Marckwald and the author (*Ber.*, 1901, **34**, 485) have recently separated the alcohols of fusel oil by converting them into the crystalline β-acid esters of 3-nitrophthalic acid. Inactive 1-*iso*amyl-3-nitrophthalic acid and 1-*d*-amyl-3-nitrophthalic acid were isolated, and the corresponding alcohols, *iso*butylcarbinol, $(CH_3)_2CH\cdot CH_2\cdot CH_2\cdot OH$, and *l*-methylethylcarbincarbinol, $CH_3\cdot(C_2H_5)CH\cdot CH_2\cdot OH$, were obtained from them on hydrolysis. We noticed, in the course of the work, that (1) when 3-nitrophthalic acid was esterified by amyl alcohol by E. Fischer and Speier's method, the main product was the β-acid ester, but the α-acid ester and the normal ester were also formed, (2) when the alcohol was directly esterified by 3-nitrophthalic anhydride, the main product was the α-acid ester, the β-acid ester being also present. Wegscheider and Lipschitz (*loc. cit.*) have shown that when the acid is esterified in presence of sulphuric acid and methyl alcohol, the main product is the β-acid ester, but the normal ester is also produced under certain conditions. Direct esterification by the anhydride, on the other hand, was found by them to yield 90 per cent. of the α-compound.

Isomeric acid esters of the type under consideration vary in electrical conductivity, and Wegscheider has shown this in several cases, for example,



α-Ester ($\kappa = 0{\cdot}2$).



β-Ester ($\kappa = 1{\cdot}5$).

In fact, Wegscheider bases his nomenclature of such compounds on the difference in conductivity, that ester with the smaller value for κ being termed the α-ester (*Monatsh.*, 1895, **16**, 141, &c.). Of the two carboxyl groups in 3-nitrophthalic acid, the one in the ortho-position

relatively to the nitro-group is the "stronger" of the two, and the stereochemical obstruction caused by it is more marked than that caused by the other group in the 1-position. Therefore on esterification by the hydrogen chloride or sulphuric acid method, the β-acid ester is the main product. According to this view, both isomerides might be expected to be formed, the relative amounts of which would depend on the difference between the carboxyl groups in the particular acid used. The present paper affords evidence for the formation of both isomerides on the esterification of an unsymmetrical dicarboxylic acid, a probability which has been repeatedly suggested by Wegscheider (*Monatsh.*, 1895, **16**, 141; 1897, **18**, 640; 1899, **20**, 696; *Oesterr. Chem. Zeit.*, 1901, 6; *Ber.*, 1901, **34**, 680). The formation of the normal ester on esterification by the sulphuric acid method was also observed. Further, inactive 2-*iso*amyl-3-nitrophthalic acid and 2-*d*-amyl-3-nitrophthalic acid have been prepared and examined.

For the preparation of 3-nitrophthalic acid, the method by nitration of phthalic acid (Miller, *Annalen*, 1881, **208**, 225) is most convenient. On nitrating, care should be taken to observe just when the action begins, and at once to moderate it by cooling, otherwise it proceeds too violently. The melting point of the acid used in the following experiments agreed with that of Miller.

3-*Nitrophthalic Anhydride.*

The following was found a suitable means of preparation. Equal weights of the acid and acetic anhydride are gently heated with the free flame until all the acid dissolves, and then for five minutes longer to complete the reaction. When the solution cools, the anhydride quickly crystallises, and is drained off and washed with ether. It melts at 162°. A further quantity may be obtained from the mother liquor on removal of the ether and the bulk of the acetic anhydride. The method gives an almost theoretical yield.

2-iso*Amyl*-3-*nitrophthalic Acid.*

The corresponding β-acid ester, which yielded *iso*butylcarbinol, has already been described (Marckwald and McKenzie, *loc. cit.*). The α-compound was prepared by heating *iso*butylcarbinol (4·5 grams) with a 5 per cent. excess of nitrophthalic anhydride (9·4 grams) for 15 minutes on the water-bath, and then carefully for 5 minutes with the free flame. After addition of benzene to the hot solution, a finely crystalline crop of 8·5 grams separated on cooling, and when this was recrystallised several times from benzene it melted at 165—166°. On analysis:

0·5704, dried at 100° and dissolved in methyl alcohol, required 20·35 c.c. *N*/10 potassium hydroxide for neutralisation. $C_{13}H_{15}O_6N$ requires 20·30 c.c.

The ester is sparingly soluble in benzene and carbon tetrachloride, and is hydrolysed with much more difficulty than the β-isomeride. On theoretical grounds, the latter observation was to be expected, as the alcohol radicle in the α-ester is regarded as replacing the hydrogen of the stronger carboxyl group, and should therefore not be so easily detached as in the case of the β-ester.

2-d-*Amyl*-3-*nitrophthalic Acid.*

The corresponding β-ester has been described (*loc. cit.*). An acetone solution of it gave $[\alpha]_D^{17°}$ +6·5° ($c=10$), and the *l*-amyl alcohol obtained from it had the rotation $\alpha_D^{20°}$ −9·62°; hence $[\alpha]_D^{20°}$ −5·90°.

The amyl alcohol used for the preparation of the α-ester was prepared by subjecting fusel oil (α_D −2·2°, $l=2$) to a modification of the Le Bel-Rogers' method, and then working up the product (α_D −6°, $l=2$) by treatment with 3-nitrophthalic acid (*loc. cit.*). A prolonged series of crystallisations yielded an ester with the rotation in acetone $[\alpha]_D^{22°}$ +5·9° for $c=10$, but in this case the separation of the mixed crystals was not carried to the limit. The product, on hydrolysis, gave an alcohol with $\alpha_D^{26°}$ −8·50° ($l=2$), which contained therefore 88·5 per cent. of *l*-amyl alcohol.

This alcohol (9·8 grams) was heated with a 5 per cent. excess of nitrophthalic anhydride (20·5 grams) for 25 minutes on the water-bath, and then carefully with the free flame until the solution was clear. After treatment with benzene as before (p. 1137), 19·2 grams were obtained with the m. p. 156—158° and with the rotation in acetone solution $[\alpha]_D^{26°}$ +2·2° for $c=8·3615$. After recrystallisation from benzene, 17·9 grams (m. p. 157·5—158·5°) resulted, and a determination of the specific rotation in acetone solution gave the following result:

$$l=2,\ c=8·256,\ \alpha_D^{21°}\ +0·37°,\ [\alpha]_D^{21°}\ +2·2°.$$

On analysis:

0·3945, dried at 100° and dissolved in methyl alcohol, required 14·4 c.c. *N*/10 potassium hydroxide for neutralisation. $C_{13}H_{15}O_6N$ requires 14·04 c.c.

0·1939 gave 0·0925 H_2O and 0·3985 CO_2. H = 5·3; C = 56·0.
$C_{13}H_{15}O_6N$ requires H = 5·3; C = 55·5 per cent.

Like the isomeric β-ester, this compound is beautifully crystalline. It dissolves at once in cold dilute ammonia solution, is very easily soluble in acetic ether or acetone, and easily in chloroform, but only

sparingly in benzene or carbon disulphide. It is hydrolysed with more difficulty than the β-ester. Its melting point was not raised on recrystallisation from benzene and from other solvents.

Esterification of Amyl Alcohol by Nitrophthalic Anhydride.

This experiment indicates the formation of α- and β-acid esters.

An active amyl alcohol (33 grams, a 5 per cent. excess) with the rotation α_D −4·7° ($l=2$) was heated on the water-bath for 15 minutes with nitrophthalic anhydride (69 grams) until the mass became a solid paste, which was then cautiously heated with a free flame until the solution was clear. By treatment with benzene as before, and after recrystallisation of the resulting product from benzene, 55 grams were obtained; this, on analysis, had the composition $C_{13}H_{15}O_6N$. The specific rotation in acetone was $[\alpha]_D^{17°}$ +1·1° ($c=8·1155$). The product contained no normal ester, as it dissolved at once in cold dilute ammonia; it melted at 151—154°, and an examination of the melting points of successive crops from benzene and other solvents showed that it obviously presented a case of mixed crystals of the acid esters containing the α-compound in excess. The separation would have proved very tedious, and was not in this case carried out. Systematic crystallisation of the benzene mother liquors yielded a product containing excess of the β-ester, and crystallising from carbon disulphide in glassy, transparent prisms (m. p. 101—110°); a determination of its rotation in benzene gave $[\alpha]_D$ +5·9° for $c=3·5655$.

Esterification of Amyl Alcohol by Nitrophthalic Acid.

This experiment affords evidence for the production of α- and β-acid esters, and of the normal ester.

The amyl alcohol used had the rotation α_D −6° ($l=2$), and contained therefore about 60 per cent. *l*-amyl alcohol.

3-Nitrophthalic acid (89 grams) was heated on the water-bath for 14 hours with amyl alcohol (178 grams) and sulphuric acid (26·7 grams). When the bulk of the mineral acid had been removed by washing with water, the amyl alcohol was separated by distillation under diminished pressure, and further esterified as before, in order to obtain a larger yield of crystalline esters. The alcohol removed after each esterification was markedly less lævorotatory than the original and this indicated that the active constituent was esterified more quickly than the inactive. The brown oil obtained from the two esterifications was warmed, and an excess of carbon disulphide added. After several hours, the crystals were drained off and washed with carbon disulphide. In this way, 80 grams of a mixture of the acid

esters were obtained, from which 1-*d*-amyl-3-nitrophthalic acid may be separated (*loc. cit.*).

From the carbon disulphide mother liquors, the carbon disulphide and the free amyl alcohol were removed by distillation in a current of steam. A calculated excess of sodium hydroxide was added to the residue, and the distillation in steam was continued until no more alcohol was observed to distil over. The residue in the flask, although alkaline, contained a heavy oil, which was separated, and proved to be the normal ester, and could only be hydrolysed with difficulty. The amyl alcohol obtained from it by heating it with 33 per cent. sodium hydroxide and then distilling in steam, weighed 22 grams, and had the rotation $\alpha_D - 5{\cdot}83°$ ($l = 2$).

For the formation of normal ester, compare Wegscheider and Lipschitz (*loc. cit.*), and Graebe and Rostowzew (*Ber.*, 1901, **34**, 2107).

Esterification of Methyl Alcohol by Nitrophthalic Anhydride.

Nitrophthalic anhydride (38 grams) was heated on the water-bath under a reflux condenser for 2 hours with methyl alcohol (100 c.c.). After standing overnight, the alcohol was evaporated off, and a crystalline solid was obtained which was sparingly soluble in cold, but much more easily in hot water. A small portion of it dissolved at once in cold dilute ammonia, and therefore no normal ester was present. After one crystallisation from water, the air-dried substance weighed 40 grams, and a sample of it, dried at 100°, melted very slightly between 138° and 145°, and mainly between 145° and 149°. By repeated crystallisation, each time from much water, the melting point became very gradually sharper, whilst each crystallisation yielded glassy, prismatic needles, apparently uniform in crystalline form. The variations in melting point undoubtedly showed that the case was one of mixed crystals of the α- and β-acid esters, with the former in excess. The difficulty of separating the constituents of the mixture in such a case is exemplified by the experience of Balbiano (*Gazzetta*, 1876, **6**, 229), and of Marckwald and the author (*loc. cit.*).

The isolation of the α-compound was conducted by recrystallising the above product 25 times from water; the progress of the separation was observed by a determination of the melting point of each successive crop, dried at 100°. The sulphuric acid, in which the melting point tube was immersed, was kept in constant agitation, and the temperature, when near the melting point, was not allowed to rise more than 1° per minute. The points at which melting was just observable, and at which the last trace of solid had disappeared, were carefully noted by aid of a lens. The melting points

were not corrected. Finally, 4 grams of the α-compound were obtained, the melting point of a portion of which, dried at 100°, was 152—153°. On analysis:

0·6237, dried in air, lost 0·0480 at 105°. $H_2O = 7·7$.

$C_9H_7O_6N + H_2O$ requires $H_2O = 7·4$ per cent.

0·5757 anhydrous substance, dissolved in methyl alcohol, required 25·7 c.c. $N/10$ potassium hydroxide for neutralisation.

$C_9H_7O_6N$ requires 25·6 c.c. per cent.

Wegscheider and Lipschitz (*Monatsh.*, 1900, 21, 794), under different conditions from those just described, claim to have obtained a 90 per cent. yield of the α-ester, and give its melting point as 144°. On repetition of the esterification exactly under the conditions quoted by them, I was unable to confirm their results. The phenomenon of mixed crystals was again evidenced. The α-ester was, however, isolated, and melted as before at 152—153°.

On esterification of methyl alcohol by 3-nitrophthalic acid by the E. Fischer-Speier method and removal of the small amount of normal ester produced, a product was obtained which melting point determinations again indicated to consist of mixed crystals of the α- and β-acid esters. The separation of the β-ester was, however, not attempted.

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CXXII.—*Derivatives of 3-Nitrotolyl-4-hydrazine.*

By FRANK GEO. POPE and JAS. MORTON HIRD.

SOME years ago, one of the authors, in conjunction with J. T. Hewitt, described *m*-bromo-*p*-tolylhydrazine and its derivatives (Trans., 1898, 73, 174), from which it was thought that closed ring compounds might be produced by elimination of halogen from the nucleus and hydrogen from the side chain. At the time, however, no satisfactory results were obtained, although by the action of heat on the anhydrous potassium salt of the pyruvic acid hydrazone, two substances, one being acidic in character and the other phenolic, were formed. Their nature was not further determined at the time, and experiments are still being carried on in the hope of eliminating hydrogen bromide from the compounds.

It has occurred to us that the corresponding nitrohydrazine might be more suitable for the formation of such closed rings, and experi-

ments are now being carried out in this direction, but as none has yet been brought to a perfectly definite conclusion, we think it advisable to give a short account of the preparation and properties of the hydrazine and some of its chief derivatives.

For the purpose of obtaining the hydrochloride of this hydrazine from *m*-nitro-*p*-toluidine, V. Meyer and Lecco's method (*Ber.*, 1883, **16**, 2976) was employed. The double tin salt of the hydrazine was freed from tin by hydrogen sulphide; on filtering off the precipitated tin sulphide and carefully evaporating the solution, the hydrazine hydrochloride was obtained in orange-red plates or needles. The recrystallised salt melts and decomposes at 190—191°, and is soluble in water with slight decomposition. In aqueous solution, the salt shows the characteristic reduction of Fehling's solution. On analysis:

0·0872 gave 15·8 c.c. nitrogen at 18° and 744·5 mm. N = 20·36.
$C_7H_{10}O_2N_3Cl$ requires N = 20·68 per cent.

The hydrazine is obtained from a solution of the hydrochloride in water, by the addition of sodium acetate, as a dark red precipitate. This, after being dried over sulphuric acid and recrystallised from ether, separates in dark red tufts of needles melting at 110°. On analysis:

0·0949 gave 20·5 c.c. nitrogen at 19° and 757 mm. N = 24·80.
$C_7H_9O_2N_3$ requires N = 25·15 per cent.

The base is very soluble in acetone, and moderately so in ether, ethyl acetate, chloroform, or benzene, but only slightly so in light petroleum.

Pyruvic acid nitrotolylhydrazone, $NO_2{\cdot}C_7H_6{\cdot}NH{\cdot}N{:}C(CH_3){\cdot}CO_2H$, is precipitated immediately on mixing aqueous solutions of the hydr azine hydrochloride and pyruvic acid as a chrome yellow, amorphous substance. This, when recrystallised from alcohol, melts at 203° with decomposition. It is soluble in acetone, ether, ethyl acetate, benzene, or chloroform, but only slightly so in light petroleum. On analysis:

0·1024 gave 16·1 c.c. nitrogen at 25° and 747 mm. N = 17·50.
$C_{10}H_{11}O_4N_3$ requires N = 17·72 per cent.

The *ethyl ester*, $NO_2{\cdot}C_7H_6{\cdot}NH{\cdot}N{:}C(CH_3){\cdot}CO_2C_2H_5$, was prepared by boiling the hydrazone with its own weight of sulphuric acid and ten times its weight of absolute alcohol for 10 hours in a reflux apparatus. The mixture was then poured into dilute sodium carbonate solution, when the ester separated in yellow flocks, which, on crystallisation from alcohol, formed small, orange needles melting at 140°. On analysis:

0·1353 gave 18·9 c.c. nitrogen at 24° and 768 mm. N = 15·79.
$C_{12}H_{15}O_4N_3$ requires N = 15·85 per cent.

Nitrotolylsemicarbazide, $NO_2 \cdot C_7H_6 \cdot NH \cdot NH \cdot CO \cdot NH_2$, is immediately precipitated on mixing aqueous solutions of the hydrazine hydrochloride (2 grams) and potassium cyanate (0·81 gram) as a light yellow, sandy powder. This, when recrystallised from much hot water, in which it is only slightly soluble, is obtained in small, yellow needles which melt at 201° with decomposition, and are only slightly soluble in the usual solvents. On analysis:

0·1449 gave 33·9 c.c. nitrogen at 25° and 751 mm. N = 26·44.
$C_8H_{10}O_3N_4$ requires N = 26·67 per cent.

An aqueous solution of this substance, on treatment with alcoholic potash in the cold, gives a deep violet colour, and if left to stand for some days, a crystalline precipitate is obtained.

Salicylaldehyde nitrotolylhydrazone, $NO_2 \cdot C_7H_6 \cdot NH \cdot N{:}CH \cdot C_6H_4 \cdot OH$, was obtained in the following manner: 1·25 grams of salicylaldehyde were covered with water, and 2 grams of the hydrazine hydrochloride, dissolved in water, added; the whole was then well shaken after the addition of excess of sodium acetate solution. A brilliant scarlet precipitate was immediately produced; this was recrystallised from benzene, in which it is very soluble, separating in the form of needles which melt at 226°. It dissolves only sparingly in ether, ethyl acetate, chloroform, or light petroleum. On analysis:

0·1083 gave 15·1 c.c. nitrogen at 20° and 737 mm. N = 15·46.
$C_{14}H_{13}O_3N_3$ requires N = 15·50 per cent.

Furfuraldehyde nitrotolylhydrazone, $NO_2 \cdot C_7H_6 \cdot NH \cdot N{:}CH \cdot C_4OH_3$ was obtained in an analogous manner, giving a bright scarlet precipitate, which was recrystallised from hot alcohol, forming red needles melting at 165—166°. It dissolves easily in the ordinary organic solvents except ether and light petroleum. On analysis:

0·1285 gave 19·6 c.c. nitrogen at 15° and 755 mm. N = 17·75.
$C_{12}H_{11}O_3N_3$ requires N = 17·14 per cent.

Benzaldehyde nitrotolylhydrazone, $NO_2 \cdot C_7H_6 \cdot NH \cdot N{:}CH \cdot C_6H_5$, was also obtained in the same manner, and crystallised from benzene in red needles which melted at 166°. It is only slightly soluble in light petroleum or acetone. On analysis:

0·0996 gave 15·2 c.c. nitrogen at 26° and 759 mm. N = 16·74.
$C_{14}H_{13}O_2N_3$ requires N = 16·47 per cent.

Phenylnitrotolylthiosemicarbazide, $NO_2 \cdot C_7H_6 \cdot NH \cdot NH \cdot CS \cdot NH \cdot C_6H_5$, was prepared by mixing ethereal solutions of the free hydrazine and

phenylthiocarbimide in molecular proportion, and allowing the solution to stand for about half an hour. When recrystallised from ether, it gave tufts of golden yellow needles melting and decomposing at 188°. On analysis:

0·1010 gave 16·8 c.c. nitrogen at 17° and 750 mm. N = 18·91.
$C_{14}H_{14}O_2N_4S$ requires N = 18·54 per cent.

Nitrotolylallylthiosemicarbazide, $NO_2 \cdot C_7H_6 \cdot NH \cdot NH \cdot CS \cdot NH \cdot C_3H_5$, was prepared in a similar way, and formed yellow needles melting at 168—170° when recrystallised from dilute alcohol. On analysis:

0·1120 gave 21 c.c. nitrogen at 28° and 759 mm. N = 21·0.
$C_{11}H_{14}O_2N_4S$ requires N = 21·52 per cent.

Acetylnitrotolylhydrazine, $NO_2 \cdot C_7H_6 \cdot NH \cdot NH \cdot CO \cdot CH_3$, was prepared by boiling the hydrazine with an excess of glacial acetic acid for 4 hours in a reflux apparatus, pouring the product into water, filtering, washing with cold water, and recrystallising from hot water. It formed small, golden needles melting at 161°. On analysis:

0·1012 gave 17·5 c.c. nitrogen at 19° and 768 mm. N = 20·25.
$C_9H_{11}O_3N_3$ requires N = 20·10 per cent.

We hope to be able to communicate further results as to the behaviour of certain of these compounds shortly.

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CXXIII.—*The Constituents of the Sandarac Resins.*

By Thomas Anderson Henry, D.Sc.(Lond.), Salters' Company's Research Fellow in the Laboratories of the Imperial Institute.

The sandarac of commerce is derived from the plant *Callitris quadrivalvis* which occurs in the plant family *Cupressineæ*, a subdivision of the *Coniferæ*. Like most plants of this order, the various species of *Callitris* secrete an oleo-resin, which at certain seasons of the year exudes from the stem, and by evaporation of a portion of its contained volatile matter forms small, hard masses of resin technically known as "tears." It is in this form that sandarac occurs in commerce, the "tears" being long and narrow, having a glassy fracture, and a pungent, aromatic, and slightly bitter taste. The resin is employed in the manufacture of some of the finer kinds of spirit varnishes, and in the form of a powder for dusting on the surface of parchment to increase its absorptive power for ink.

There also appears on the market from time to time a similar resin, which, since it is exported from Australia, is commonly known as "white pine resin," or "Australian sandarac." This substance is the natural exudation product of *Callitris verrucosa*, and differs from the common sandarac chiefly in the larger size of its "tears" and its smaller solubility in alcohol.

It was with the object of comparing the constituents of these two resins that the present investigation was undertaken.

The chemical constituents of the resins of the various species of *Pinus* have been the subject of many investigations, but the less known members of the *Coniferæ* have been somewhat neglected in this respect, so that the literature of the present subject is meagre.

The first important paper dealing with the chemistry of sandarac is that of Johnston (*Phil. Trans.*, 1839, 129, 239), who asserts that the resin contains three acids differing in their solubilities in alcohol and in those of their potassium salts in alcoholic potash. These acids were isolated in the following way. The resin was exhausted with alcohol, leaving an insoluble, yellow, amorphous powder, soluble in ether and having a composition represented by the formula $C_{40}H_{31}O_5$. This the author calls A resin. The alcoholic extract was then treated with solid potash, whereby an insoluble potassium salt was obtained. This, on solution in water and addition of hydrochloric acid, gave B resin, which is similar in appearance to the A resin, but is soluble in alcohol, and has a composition represented by the formula $C_{40}H_{31}O_6$. The portion soluble in alcoholic potash gave, on regeneration with acids, a mixture of two resins, of which one, soluble in alcohol and on combustion giving numbers corresponding with those required for the formula $C_{40}H_{30}O_6$, is named C resin; whilst the other, insoluble in alcohol, is regarded as identical with A. No attempts were made by the author to crystallise these substances, nor were any well-defined derivatives obtained from them.

The only other paper of interest is that of Tschirch and Balzer (*Arch. Pharm.*, 1896, 234, 291). These authors adopted a slight modification of Johnston's method for the separation of the constituents, namely, they dissolved the resin in aqueous potash, and to this solution added solid potash, so precipitating an insoluble potassium salt, from which was regenerated, by solution in water and addition of hydrochloric acid, an amorphous resin which was named *sandaracolic acid*. This substance is said to be obtained in a crystalline condition by allowing its alcoholic solution to stand for a long time. The crystals melted at 140°, and on combustion numbers were obtained agreeing with those required by the formula $C_{45}H_{66}O_7$. The molecular weight was determined by Raoult's freezing point method, and the curious results obtained by the authors are tabulated below. In calculating M from

the experimental data, evidently some arithmetical error has been made by the authors, as is shown by the recalculated values of M given in the tabular statement ($C_{45}H_{66}O_7$ requires M = 718).

Weight of solvent used (phenol).	Weight of substance used.	Depression of freezing point.	Molecular weight calculated by Tschirch and Balzer.	Molecular weight recalculated.
28·85	0·255	1·00°	660	65
25·102	0·200	0·49	645	120
25·10	0·260	0·12	690	638

Such arithmetical errors frequently occur throughout the paper, and will be pointed out as they arise. By titration experiments with normal potash, the authors find that this acid is monobasic, yet they assign without comment to the copper salt, obtained by double decomposition between copper sulphate and the sodium salt, a formula representing it as that of a dibasic acid, namely, $C_{45}H_{64}O_7Cu$. The silver salt was also prepared by the addition of excess of ammonia to sandaracolic acid and the further addition of ammoniacal silver nitrate solution. On standing for some weeks, this solution deposited a precipitate which was found to contain 12·84 per cent. of silver; $C_{45}H_{65}O_7Ag$ requires 13 per cent. By the action of acetic and benzoic anhydrides, monoacetyl and monobenzoyl derivatives respectively were obtained, but only in an amorphous condition. By the action of hydriodic acid in Zeisel's apparatus, evidence of the existence of a methoxyl group in the acid was obtained, whilst oxidation with nitric acid gave picric and oxalic acids. Fusion with potash gave a substance resembling resorcinol. From the potassium salt soluble in excess of potash, was isolated by the addition of hydrochloric acid, a second resin, to which the name callitrolic acid was given. This acid was with difficulty obtained in a crystalline condition by conversion into its amorphous lead salt and regeneration by sulphuretted hydrogen. The crystallised acid melted at 248°, and, on combustion, the following results were obtained:

(i) C = 77·79, H = 8·63; (ii) C = 77·58, H = 8·30.

$C_{65}H_{84}O_8$ requires, according to the authors' calculations, C = 77·3, H = 8·43 per cent.

In reality, this formula requires C = 78·6, H = 8·4 per cent., and the results obtained by the authors are better represented by the formula $C_{62}H_{80}O_8$, where C = 78·15, H = 8·40 per cent.

The molecular weight was determined by the freezing point method, and found to agree with that required by the formula $C_{65}H_{84}O_8$. The

same carelessness in calculation is shown here, thus: 22·14 grams of phenol, containing 0·331 gram of the acid, gave a depression 0·12°. According to the authors, this corresponds to a molecular weight 952; in reality, the calculated value is 921, but this is sufficiently near that required by the formula $C_{65}H_{84}O_8$ to be within experimental error. Callitrolic acid was also found to be monobasic, yet the authors assign to its copper salt the formula $C_{65}H_{82}O_8Cu$, which is that of a salt of a dibasic acid. On subjecting the crude resin to steam distillation, a quantity of a brown oil having an odour of pine trees was obtained, but was not further examined. Since the appearance of the above paper, Tschirch, in a note appended to a paper on another subject, mentions that he has isolated from sandarac a new crystalline acid by shaking an ethereal solution of the resin with sodium carbonate (Dieterich, *Analyse der Harz*, *Berlin*, 1900), but no further information regarding this acid has been published.

It will be convenient to include in this account of previous work on this subject a short *résumé* of the work so far accomplished on pine resins, since, as will be seen later, the constituents of sandarac bring it into close relation with this class.

From commercial colophony there have been isolated by various workers, *sylvic*, *sylvinic*, iso*sylvinic*, *pimaric*, *pinic*, and *abietic* acids, but the researches of Liebermann (*Ber.*, 1884, 17, 1884), Haller (*Ber.*, 1885, 18, 2165), Maly (*Annalen*, 1869, 149, 115, 161, 244), and especially of Mach (*Monatsh.*, 1893, 14, 186; 1894, 15, 627), show clearly that most of these substances are merely impure forms of abietic acid. Mach examined a large number of specimens of American and French colophony and of "galipot," and in each case he was only able to isolate *abietic acid*, $C_{19}H_{28}O_2$. On the other hand, Vesterberg, in his researches on the constituents of "colophonium de Bordeaux" (*Ber.*, 1885, 18, 3331; 1886, 19, 2167; 1887, 20, 3251), found that this resin contained two isomeric crystalline acids of the formula $C_{20}H_{30}O_2$, to which he gave the names d- and l-*pimaric acids*. Whilst Mach could not obtain these substances from the Bordeaux colophony now obtainable in commerce, he was able, by an examination of a specimen of *d*-pimaric acid supplied to him by Vesterberg, to confirm the results of the latter.

These results are perhaps to be explained on the assumption that American colophony has, in European commerce, almost replaced the French product, whilst the American "thus" is now commonly sold in place of "galipot."

In a more recent investigation of Bordeaux turpentine by Tschirch and Bruenig (*Chem. Centr.*, 1900, ii, 1270), it was found that this resin contains two crystalline acids, pimarinic acid (m. p. 114—118°) and pimaric acid. The latter, isolated by treating the resin with soda

solution, was optically inactive, whilst the pimaric acid, isolated from a specimen of Bordeaux colophony by crystallisation from alcohol, was strongly lævorotatory. The optical inactivity of the first-mentioned specimen of acid is accounted for by the authors on the assumption that racemisation occurs with the conversion into the sodium salt. These results are in direct opposition to those of previous workers—thus, Vesterberg used the sodium salts of *d*- and *l*-pimaric acids as a means of isolating and purifying these substances, and the products so obtained were optically active. Further, it should be pointed out that, although the authors give a certain amount of evidence for the statement that pimarinic acid is a new substance, they content themselves as regards pimaric acid with the assertion that they obtained it, and give no details as to how they identified it. Since no account of an inactive pimaric acid has, so far, appeared in chemical literature, it is curious that no attempt was made to characterise this substance when opportunity offered.

Attention should also be drawn to the work of Bruylants on the destructive distillation of colophony (*Ber.*, 1875, **8**, 1463; 1878, **11**, 447). This author obtained in this way ethylene, propylene, and amylene, and by the destructive distillation of calcium pimarate, similar compounds, together with methyl ethyl ketone, diethyl ketone, toluene, dimethylbenzene, terebene, and diterebene. He infers from these observations that the constitution of pimaric acid may be represented by the formula

$$C_3H_7 \cdot C_6H_6(CH_3) \cdot C_6H_6(CH_3) \cdot C_2H_4 \cdot CO_2H,$$

which is that of a carboxyl derivative of a diterpene.

In a similar manner, Bischoff and Nastvogel (*Ber.*, 1890, **23**, 1921) obtained, by destructively distilling colophony in a vacuum, an oily hydrocarbon boiling at 216—225°, and a volatile resin to which they give the name iso*sylvinic anhydride*, since, on treatment with sodium hydroxide, it gave the sodium salt of an acid isomeric with sylvinic acid, $C_{20}H_{30}O_2$. To the oily hydrocarbon which they regarded as identical with the colophene of Deville (*Ann. Chim. Phys.*, 1840, [ii], **75**, 37) and Riban (*Ann. Chim. Phys.*, 1875, [v], **6**, 40), they ascribe a constitution, which is that of a condensed dihydrocymene, whilst they further represent *iso*sylvinic acid as a carboxy-derivative of colophene, and the anhydride as formed by the condensation of two molecules of the acid.

It will be seen that such a formula closely resembles that suggested by Bruylants. Similar evidence of the aromatic character of the nucleus of the acid of colophony is given by Ciamician, who obtained, by distillation of this resin with zinc dust (*Ber.*, 1878, **11**, 269), such substances as toluene, naphthalene, methylnaphthalene, and methyl-

anthracene. Further, Wallach and Rheindorff (*Annalen*, 1892, 271, 285) find that colophony, on destructive distillation, yields pinene and dipentene.

Experimental.

Extraction of the Volatile Oil.

The crude resin was dissolved in alcohol, and the solution made alkaline by the addition of alcoholic potash in slight excess. The alcohol was then removed by distillation, the residual semi-solid mixture of potassium salts dissolved in water, and the solution shaken out with ether. Preliminary experiments having shown that the volatile oil of the plant consisted only of hydrocarbons, the ethereal solution so obtained was next dried over solid potash, which removed, besides water, a small amount of resinous matter. The ether was then removed by distillation, and the residue fractionally distilled. In general, it was separated into three portions, having the following range of boiling points: 150—180°, 180—220°, and 220—280°. From the first of these, a large fraction boiling from 150—160° could be obtained, which on redistillation over metallic sodium gave a portion boiling from 152—159°. The fraction 180—220° evidently was a mixture, but it was found impossible to get even a partial separation of its constituents, since on distillation the temperature rose fairly rapidly and regularly between the two limits mentioned. The fraction 220—280°, on rectification over metallic sodium, came over mostly from 260—280° as a slightly viscous, colourless oil, having an odour faintly recalling that of peppermint. With the small quantities of volatile oil obtainable, it was impracticable to attempt by further fractionation to obtain purer products than these two fractions. Their examination was therefore proceeded with.

Fraction boiling between 152° *and* 159°.

This fraction was a colourless liquid with a pleasant, pine-like odour. Its density at 15°/15° was 0·8588 [pinene 0·8586].

Determinations of the optical activity of the fraction in a 100 mm. tube with a Laurent's polarimeter, using sodium light, gave +18°27′ as the mean of ten observations, whence $[\alpha]_D$ +21°30′.

Action of Nitrosyl Chloride.—To a few c.c. of the fraction the same quantity of amyl nitrite was added, and sufficient glacial acetic acid to form a clear solution, which was then cooled by immersion in a mixture of sodium sulphate and hydrochloric acid. To the solution was added, drop by drop, strong hydrochloric acid so long as a blue colour was produced, which disappeared on cooling and shaking. After a few minutes, a crop of crystals separated. These were removed by

filtration, and recrystallised by addition of methyl alcohol to their chloroform solution. The substance so obtained formed silky masses of minute needles melting at 103° when heated slowly. For purposes of comparison, a specimen of pinene nitrosyl chloride was prepared from commercial turpentine by the method described above. This presented a similar appearance to that obtained from sandarac oil, and melted at the same temperature under the same conditions.

Preparation of the Nitrolpiperidide.—The nitrosyl chloride of the hydrocarbon was dissolved in a little alcohol, and a slight excess of piperidine was added to the solution, which was then warmed on the water-bath for a few minutes. To the mixture, water was added, causing the precipitation of a heavy, oily liquid. The excess of water was poured off, and the oil dissolved in alcohol and set aside. After several days, a small quantity of a substance crystallising in needles and melting at 118°, after recrystallisation from alcohol, was obtained. A specimen of pinene nitrol piperidide, obtained in like manner from pinene nitrosylchloride, melted at 118°.

The fraction of lower boiling point from sandarac oil is therefore composed chiefly of *d*-pinene.

Fraction boiling between 260° *and* 280°.

This portion of the volatile oil, when freshly distilled over metallic sodium, is a colourless, somewhat viscous liquid, but on standing it slowly assumes a greenish colour and shows slight signs of resinification. Its density at 15°/15° was 0·9386.

From its boiling point and general behaviour it was apparently a sesquiterpene or a diterpene, and further examination showed the latter supposition was most probably correct.

The oil is dextrorotatory. A determination of the specific rotation in a 100 mm. tube, using sodium light, gave +51°42′ as the mean of ten observations, whence $[\alpha]_D$ +55°.

The refractive index was determined by means of an Abbé refractometer and gave $\mu = 1{\cdot}5215$ as the mean of ten observations.

On analysis, the following result was obtained:

0·1237 gave 0·400 CO_2 and 0·128 H_2O. C = 88·1; H = 11·4.

$C_{20}H_{32}$ requires C = 88·3; H = 11·7 per cent.

A determination of the vapour density by Victor Meyer's method, using anthracene vapour as the heating agent, gave the molecular weight = 262; $C_{20}H_{32}$ requires 272.

Ethereal solutions of this hydrocarbon do not absorb hydrogen chloride, but they decolorise bromine with evolution of hydrogen bromide.

A satisfactory bromine derivative has not been obtained, the product being an oil which does not crystallise from solvents or become crystalline when kept at low temperatures. On heating, even in a vacuum, it decomposes, giving resinous products, so that no method has been found of obtaining it in a pure state.

The hydrocarbon does not combine with either nitrosyl chloride or nitrogen trioxide. In several attempts to prepare such derivatives by the usual methods no combination occurred, and the unaltered substance was recovered at the end of the experiments. On adding strong sulphuric acid, drop by drop, to a solution of the hydrocarbon in glacial acetic acid, a deep violet colour is produced, which disappears on warming.

The physical constants of this oil show that it does not belong to the class of sesquiterpenes, but probably to the diterpenes. The properties of the latter class of substances are so far but imperfectly known. The constants given in the following table are those ascribed to the few diterpenes which have been isolated. For convenience of comparison, the constants usually characteristic of the sesquiterpenes are also added:

	Relative density.	Vapour density.	Refractive index.	B. p.	Action of HCl.
Sesquiterpenes.....	0·9001—0·918	7·23	1·501	240—260°	Forms additive products.
Diterpenes.....	0·938	9·6	—	260—315	No action.
Sandarac hydrocarbon.....	0·9386	9·28	1·5215	270—280	No action.

It will be seen on comparing the constants of these various substances as given in the table that the characters of the hydrocarbon of high boiling point of sandarac oil are in general agreement with those of the diterpenes, and that it must be regarded as a member of this class of compounds.

Inactive Pimaric Acid.

The mixture of potassium salts of the resin acids, after treatment with ether for the removal of the volatile oil, was warmed to remove the dissolved ether, and to the aqueous solution a 20 per cent. solution of potash was added until no further precipitation occurred. The slimy precipitate rapidly settled to a semi-solid mass, from which the supernatant liquid could be readily poured off. The precipitated potassium salt was then dissolved in water, strong hydrochloric acid added in excess, and the semi-solid mixture poured upon a calico filter, washed free from acid, and dried in a current of warm air. When

quite free from moisture, it was treated with 90 per cent. alcohol, when it was found that a considerable portion of the resin was no longer soluble in that medium. The insoluble matter was filtered off, the filtrate made alkaline with alcoholic potash, and the solvent removed by distillation. With the residue, the precipitation of the potassium salt and the regeneration of the resin, as already described, was repeated until a resin quite soluble in alcohol was obtained. If to this alcoholic solution of the purified resin sufficient water be added to produce a slight turbidity, and the mixture be set aside for several days, a crop of crystals is obtained which when recrystallised melt at 171°. It was found more expeditious, however, to proceed in the following way. The alcoholic solution of the resin was treated with alcoholic soda and the solvent removed by distillation. The residual sodium salt was dissolved in water, and sufficient 10 per cent. aqueous sodium hydroxide added to cause a considerable precipitate to form. This mixture was then warmed on the water-bath until solution occurred. On cooling, a precipitate of the sodium salt slowly formed, which, when examined by aid of a lens, was found to consist of minute needles. This sodium salt can be recrystallised in the same way.

From this recrystallised salt the acid was then obtained by adding hydrochloric acid to its aqueous solution, filtering off the precipitate, and after washing and drying it, dissolving in alcohol and adding sufficient distilled water to render the solution faintly turbid. From this solution there separated in a few hours a colourless, crystalline substance, which, after recrystallising once or twice in the same manner, melted constantly at 171°.

The pure substance can also be prepared without the intervention of the sodium salt by taking the purified resin left after removal of the alcohol by distillation and distilling under 10—20 mm. pressure. Under these conditions, the residue distils easily and the temperature rises rapidly to 265° under 11 mm. pressure, and remains constant until the whole has passed over, condensing at first as a white, crystalline sublimate, and later, owing to the increasing temperature of the receiver, as a very viscous resin. A little care has to be exercised in carrying out this operation, as the solid acid is rather liable to block up the exit tube of the flask from which it is being distilled. The distillate obtained is at the ordinary temperature a vitreous, yellowish solid which can be left for months without showing signs of crystallisation. If, however, a little 70 per cent. alcohol be added to it, crystals immediately begin to form round the edges, and the whole mass becomes warm and crystallises rapidly. On recrystallisation, this acid melts at 171°, and is in every way similar to that obtained by the first-mentioned method. It crystallises in spreading rosettes of flat-

tened needles, is soluble in alcohol, ether, chloroform, or acetone, insoluble in water or petroleum, and slowly dissolves when warmed with aqueous alkali solutions. When a little is dissolved in a few drops of chloroform and about 1 c.c. of acetic anhydride added, the addition of a drop of strong sulphuric acid causes the formation of a transient pink coloration. This reaction is a convenient means of distinguishing the acid from abietic acid, which gives, under the same conditions, a deep purple colour fading into olive green.

The crystalline acid prepared in any of the three ways described is not optically active in alcoholic solution.

Combustions of the substance dried at 100° gave the following results:

0·1280 gave 0·374 CO_2 and 0·1083 H_2O. C = 79·6; H = 9·3.
0·1638 „ 0·4745 CO_2 „ 0·1413 H_2O. C = 78·9; H = 9·5.
$C_{20}H_{30}O_2$ requires C = 79·4; H = 9·9 per cent.

Combustions of the non-crystalline distillate were also made in order to ascertain whether this substance might not be the pimaric anhydride which has been asserted to exist.

0·1647 gave 0·4792 CO_2 and 0·1497 H_2O. C = 79·41; H = 9·96.
$C_{40}H_{58}O_3$ requires C = 81·9; H = 9·8 per cent.
$C_{20}H_{30}O_2$ „ C = 79·47; H = 9·9 „

This result shows that the distillate is merely pimaric acid in an amorphous form.

The basicity of the acid was determined by titration of the alcoholic solution of the acid with decinormal soda, using phenolphthalein as indicator. 0·0902 required 3·5 c.c. *N*/10 NaHO; whence 40 grams NaHO neutralise 301 grams of acid. $C_{20}H_{30}O_2 = 302$.

Salts of Inactive Pimaric Acid.—The sodium and potassium salts are easily obtained by boiling the acid with excess of solution of the alkali. On cooling, the salt crystallises out in microscopic needles.

The *silver* salt was prepared by the addition of silver nitrate solution to an aqueous solution of the sodium salt of *i*-pimaric acid. It is an amorphous white powder which is only slowly affected by light, showing merely a slight purple coloration even after several weeks' exposure.

0·0445 gave 0·0117 Ag. Ag = 26·2.
0·1454 „ 0·0384 Ag. Ag = 26·3.
$C_{20}H_{29}O_2Ag$ requires Ag = 26·4 per cent.

Ethyl Ester.—When the silver salt of pimaric acid is added to ethyl iodide, a deep purple-red solution is formed, which becomes colourless on addition of alcohol, silver iodide being precipitated. The residue

left after removal of the solvent cannot be crystallised, but can be distilled at 280—285° under 11—12 mm. pressure. It is a slightly yellowish, hard resin.

Comparison of Abietic and Inactive Pimaric Acids.

As considerable difficulty has been found by previous workers in distinguishing between abietic and *d*- and *l*-pimaric acids, it was thought advisable to prepare specimens of abietic and *d*-pimaric acids for comparison with the acid obtained from sandarac resin.

Abietic acid was easily obtained by the solution of colophony, derived from *Pinus excelsa* grown in India, in 90 per cent. alcohol and the addition of sufficient water to render the solution turbid. After a few days, a large crop of colourless crystals was obtained. These were recrystallised in the same way, and the recrystallisation repeated until the substance melted constantly at 161° [the melting point of abietic acid is 152° (Mach), or 165° (Maly)]. The substance crystallises when pure in broad laminæ, which are colourless and possess a brilliant lustre.

The sodium salt was prepared by neutralisation of an alcoholic solution of the acid with normal soda. To the liquid so obtained, sufficient normal soda solution was added to precipitate the sodium salt, which was then collected, dried, and recrystallised from dilute soda, forming masses of minute needles.

The silver salt was prepared from the latter by double decomposition in the usual manner. It is a white, amorphous substance. On analysis, it gave the following result:

0·0564 gave 0·0158 Ag. Ag = 28·01.
$C_{19}H_{27}O_2Ag$ requires Ag = 27·4 per cent.
$C_{20}H_{29}O_2Ag$ „ Ag = 26·22 „

As has already been pointed out, Mach, in his recent investigation of the pine resins, showed that it was not possible to isolate *d*-pimaric acid from the "galipot" or French colophony of commerce. Recourse was therefore had in the present instance to Burgundy pitch, which is generally supposed to be made from the oleo-resin of *Pinus maritima*, but from three specimens examined only one and the same acid melting at 161°, identical in all respects with that obtained from the resin of *Pinus excelsa*, could be isolated; thus the silver salt, prepared as already described, gave the following result on analysis:

0·046 gave 0·0126 Ag. Ag = 27·39.
$C_{19}H_{27}O_2Ag$ requires Ag = 27·4 per cent.
$C_{20}H_{29}O_2Ag$ „ Ag = 26·4 „

The attempt to prepare *d*-pimaric acid was therefore abandoned.

The differences between the pimaric acid isolated from sandarac and abietic acid may be grouped thus :—

Inactive pimaric acid, $C_{20}H_{30}O_2$.	Abietic acid, $C_{19}H_{28}O_2$.
Melts at 171°.	Melts at 161°.
Optically inactive.	$[\alpha]_D$ +66°.
Crystallises in needles.	Crystallises in laminæ.
A solution in chloroform and acetic anhydride gives a pink colour with concentrated sulphuric acid.	A solution in chloroform and acetic anhydride gives a violet colour fading to olive green with concentrated sulphuric acid.
Distils unchanged at 265° under 11 mm. pressure.	Distils unchanged at 259° under 20 mm. pressure.

Action of Bromine.—When a chloroform solution of bromine is gradually added to pimaric acid dissolved in the same solvent, the bromine is absorbed, and no hydrogen bromide is formed until the equivalent of two atoms of bromine per molecule has been added. On removing the chloroform by spontaneous evaporation, an oily substance is left, which, when dissolved in hot alcohol, deposits a colourless, granular bromine derivative on cooling. This substance has so far resisted all attempts to crystallise it.

The acid is not attacked by fused potash. After heating for 20 minutes at 200°, a considerable proportion of the acid was recovered unchanged, whilst only resinous products were formed from the remainder.

Action of Hydriodic Acid.—When the acid is heated in sealed tubes at 200—210° for 4 hours with excess of fuming hydriodic acid, it is completely reduced, forming an oily hydrocarbon. The product was made alkaline, when a small amount of iodoform was precipitated. The mixture was then shaken with ether, the ethereal solution separated, dried over solid potash, and the solvent removed by distillation. The brownish, oily residue was then distilled under 11—12 mm. pressure, and the fraction boiling between 170° and 190°, constituting about 90 per cent. of the whole, collected. This was then distilled over sodium, and after repeating this treatment twice, the oil boiled almost entirely between 180° and 185° under 11 mm. pressure. It forms a faintly yellow, oily liquid with a bluish fluorescence and has an odour recalling that of the crude higher paraffins. Its density at 15°/15° is 0·967. It is optically inactive, rapidly resinifies on exposure to air, decolorises bromine in ethereal solution, and does not absorb hydrogen chloride. It decomposes slightly when distilled under atmospheric pressure.

On combustion, the following result was obtained :

0·1237 gave 0·406 CO_2 and 0·128 H_2O. C = 88·9 ; H = 11·5.
$C_{20}H_{32}$ requires C = 88·3 ; H = 11·7 per cent.

The refractive index for sodium light was determined, using a small, hollow prism of refracting angle 61°25′. The angle of minimum deviation was found as the mean of ten observations to be 40°53′, whence $\mu = 1·5254$.

This hydrocarbon is apparently identical or isomeric with that obtained by Liebermann, Haller, and Vesterberg (*loc. cit.*), by reduction of the *d*-pimaric acid of "Bordeaux colophony" with hydriodic acid. It was suggested by Liebermann, who assigned to it the formula $C_{20}H_{32}$ or $C_{20}H_{34}$, that it was probably identical with the colophene (or colophene dihydride) obtained by Deville (*loc. cit.*) by the action of concentrated sulphuric acid on turpentine. For this substance, the name "dicamphene," as more suitably indicating its origin, has since been suggested by Armstrong and Tilden (Trans., 1879, **35**, 733). A specimen of "colophene" was prepared by the addition of strong sulphuric acid to turpentine in the proportion of 1 : 5. The volatile hydrocarbons were removed, as recommended by Armstrong and Tilden, by steam distillation, and the residual emulsion shaken with ether to remove the colophene. This solution was dried, the solvent removed in the usual way, and the residue distilled under 10—14 mm. pressure. A considerable amount of hydrocarbon came over below 100° ; the boiling point then rose rapidly to 190° and remained constant.

The portion boiling in the neighbourhood of 190° was collected and redistilled over metallic sodium, when it boiled constantly at 190° under 12 mm. pressure. This distillate is, however, not quite pure, as it always has a slight odour of camphene and of some sulphur compounds, which even repeated distillation over sodium fails to remove.

On redistillation, a few drops of distillate were obtained before the temperature became constant (206° under 35 mm. pressure), but the amount was not more than 0·1 per cent. of the whole. The observations of Armstrong and Tilden (*loc. cit.*) seem to indicate that this substance cannot be distilled even under diminished pressure, but there seems to be no difficulty in so distilling it if the pressure be sufficiently diminished. The purified substance is a viscous, slightly yellowish oil, having a camphoraceous odour which becomes somewhat pungent when warmed. It decomposes slightly when heated under the ordinary pressure, but is not decomposed even at 150° in sealed tubes. Its density at 15°/15° is 0·931.

The refractive index for sodium light was determined, using a small, hollow prism of refracting angle 61°25′. The angle of minimum deviation was found as the mean of ten observations to be 40°49′, whence $\mu = 1·5136$.

A comparison of the properties of colophene and the hydrocarbon obtained by the reduction of pimaric acid shows clearly that these two substances are not identical.

	Relative density.	Refractive index.	B. p. under 11 mm. pressure.
Colophene	0·931	1·5136	190°
Sandarac hydrocarbon.....	0·967	1·5254	180—185

Further, colophene is only slightly volatile with steam, whilst the sandarac hydrocarbon can easily be distilled in this way. The new hydrocarbon is also fluorescent, whilst colophene does not possess this property.

Action of Nitric Acid.—The acid is but slightly attacked, except by hot concentrated nitric acid, when it is converted into oxalic acid.

Oxidation by Potassium Permanganate.—When solution of potassium permanganate is added to an aqueous solution of the sodium salt of pimaric acid, decolorisation quickly occurs. The addition of the reagent was continued until the tint remained permanent for 4 hours. The solution was then filtered from manganese dioxide, and made acid by the addition of dilute sulphuric acid. A considerable amount of resin was precipitated containing some unchanged acid; this was filtered, and the filtrate distilled with steam. The distillate was distinctly acid. It was neutralised by addition of caustic soda solution evaporated to a small bulk, and silver nitrate solution was added to it. After a few minutes, a crystalline precipitate formed. This was collected and analysed, with the following result:

0·0105 gave 0·0067 Ag. Ag = 63·8.

$C_2H_3O_2Ag$ requires Ag = 64·4 per cent.

The volatile acid was therefore acetic acid.

The liquid, after distillation with steam, was shaken out with ether, the ethereal solution separated, dried over calcium chloride, and the solvent distilled off, leaving an oily residue, which, after standing for several days with occasional stirring, deposited a small quantity of minute needles. The substances melted at 260°, gave a buff-coloured bromo-componnd with bromine water, and its aqueous solution was acid to litmus paper. A sufficient quantity of this substance has not yet been obtained for its complete identification, but its properties are similar to those of trimellitic acid (m. p. 262°), which has already been found to occur among the oxidation products of crude pine resin.

Callitrolic Acid.

This is the name given by Tschirch and Balzer to the acid whose potassium salt is soluble in excess of an aqueous solution of potash, but it is used in this paper to denote the second resin acid of sandarac.

When the strongly alkaline solution of the potassium salt of callitrolic acid, obtained during the isolation of pimaric acid, is acidified with concentrated hydrochloric acid, almost the whole of the resin precipitated is insoluble in alcohol. This precipitate was boiled with alcohol until nothing more dissolved, and then treated with alcoholic potash, in which it dissolved completely. The solvent was removed by distillation, the residue dissolved in water, and more potash added. It was found that by slowly concentrating this liquid the potassium salt could be precipitated in fractions, the later fractions being nearly free from colour. These were collected, dried, and the acid regenerated by addition of acetic acid. Many attempts were made to crystallise this substance by addition of water, benzene, petroleum, &c., to its solutions in alcohol and ether, by fractional precipitation, and by purification through the lead salt, but to no purpose.

Attention was therefore turned to the preparation of derivatives, in the hope that they might be more easily crystallised, and eventually a crystalline sodium salt was obtained by dissolving the acid in absolute alcohol, and adding to that solution alcohol in which metallic sodium had been dissolved. In this way, a precipitate of the sodium salt was obtained in the form of microscopic needles. If, however, any attempt was made to remove and dry this salt, it absorbed water and formed a transparent jelly, even if the whole mixture was poured on a porous tile and the latter at once placed in a vacuous desiccator over calcium chloride. Experiments made with other salts were no more satisfactory, the potassium and ammonium salts being equally deliquescent, whilst salts of the other common metals are amorphous.

Action of Acids on Aqueous Solutions of the Alkali Salts of Callitrolic Acid.—When acids are added to aqueous solutions of the alkali salts of callitrolic acid, this acid is set free, forming a yellowish powder which may be either completely or partially insoluble in alcohol, depending on the concentrations of the acid used for the precipitation. Thus, if strong hydrochloric acid be used, the precipitate is almost insoluble in absolute alcohol, whilst if only a 10 per cent. solution of hydrochloric acid be added, a mixture of a soluble and an insoluble resin is obtained, and if acetic acid be used as the precipitating agent, the resin obtained is almost completely soluble. The *insoluble* resin

dissolves in alcoholic potash, and from this solution there can be regenerated by acetic acid a resin *soluble* in alcohol. The obvious explanation of this behaviour is, that callitrolic acid is a hydroxy-acid, which in the presence of mineral acids forms a *lactone*.

This lactone is insoluble in alcohol, acetone, ether, chloroform, benzene, or petroleum; but dissolves in hot glacial acetic acid, from which it is deposited on cooling as a granular powder, which occasionally assumes a somewhat crystalline appearance, but has never been obtained in an undoubtedly crystalline condition. If the lactone be added to concentrated alcoholic solution of inactive pimaric acid, it passes into solution, and, if the latter be diluted with alcohol, is reprecipitated as a white, granular powder.

As no crystalline derivative of callitrolic acid, except the unsatisfactory sodium salt, could be obtained, it was thought advisable to prepare specimens of the insoluble lactone in various ways, and submit these to analysis. These specimens of lactone were prepared: (*a*) by precipitation by concentrated hydrochloric acid from a specimen of freshly prepared crystalline sodium salt; (*b*) by precipitation from alcoholic solution of pimaric acid, the precipitate being washed with absolute alcohol; (*c*) by precipitation from hot glacial acetic acid solutions.

On combustion, the following results were obtained:

(*a*) 0·2065 gave 0·5802 CO_2 and 0·1747 H_2O. C = 76·6 ; H = 9·3.
(*b*) 0·2505 „ 0·6969 CO_2 „ 0·2140 H_2O. C = 76·09 ; H = 9·50.
0·1600 „ 0·4462 CO_2 „ 0·1325 H_2O. C = 76·06 ; H = 9·20.
(*c*) 0·2830 „ 0·7899 CO_2 „ 0·2415 H_2O. C = 76·14 ; H = 9·40.
0·1798 „ 0·5080 CO_2 „ 0·1490 H_2O. C = 77·03 ; H = 9·18.

$C_{30}H_{46}O_4$ requires C = 76·6 ; H = 9·7 per cent.

The composition of callitrolic acid should therefore be represented by the formula $C_{30}H_{48}O_5$, which is confirmed by a large number of analyses of the silver salt prepared from the following specimens of the lactone through the intervention of the sodium and potassium salts: (i) From lactone deposited from alcoholic solutions of pimaric acid; (ii) by solution of lactone, from acetic acid, in alcoholic potash, and precipitation with silver nitrate; (iii) by solution of lactone, from acetic acid, in alcoholic potash and fractionation by addition of excess of aqueous potash, the fractions being converted into silver salt:

(i) 0·2322 gave 0·0377 Ag. Ag = 18·02.
(ii) 0·5540 „ 0·0981 Ag. Ag = 17·7.
0·4132 „ 0·0730 Ag. Ag = 17·66.
(iii) 0·1061 „ 0·0200 Ag. Ag = 18·09.
0·1007 „ 0·0180 Ag. Ag = 17·80.

$C_{30}H_{47}O_5Ag$ requires Ag = 18·14 per cent.

Although, therefore, the composition of callitrolic acid cannot at present be definitely asserted to be that represented by the formula $C_{30}H_{48}O_5$, yet it is improbable that it is far removed from this.

The acid and its lactone are not acted on by fused potash and hot fuming nitric acid. With the latter reagent, the resin agglomerates into a semi-solid mass, and shows no sign of solution, even after warming for several days on the water-bath. An aqueous solution of the sodium salt slowly decolorises potassium permanganate, but the action soon stops unless the solution is kept hot. This is the only reaction, so far found, which seems likely to afford a method of attacking this substance. When the acid or lactone is heated with hydriodic acid in Zeisel's apparatus, no methyl iodide is formed. The acid and its lactone both react with acetic and benzoic anhydrides, with the formation of insoluble acyl compounds, which have not yet been examined.

Heating in a Vacuum.—When heated, callitrolic acid is completely decomposed, giving off carbon dioxide and an oily hydrocarbon, and leaving a hard, pitch-like residue. It was found that this operation gave a better yield of hydrocarbon when carried out under diminished pressure (360 mm.). The distillate consists of a viscous, oily liquid containing a little water, and having an odour of acetic acid. It was dissolved in ether, and the ethereal solution shaken out with dilute potash. The ethereal portion was separated, washed with water, dried over calcium chloride, and the solvent distilled off. The residue was then distilled, almost the whole passing over from 230—285°. On analysis at this stage, the oil was found to contain less than 1 per cent. of oxygen, so that it was evidently a hydrocarbon. Its further purification was therefore conducted by distillation over metallic sodium. The final product, purified in this way, boiled from 270—280°, was almost colourless when freshly prepared, but resinified slightly and became greenish on keeping, and had a faint odour of peppermint, especially when heated. In appearance and odour it closely resembled the diterpene naturally occurring in the plant, and like it gave a purple coloration when concentrated sulphuric acid was added to its solution in acetic acid. Its density at 15°/15° was 0·9303.

The hydrocarbon is optically active. Determinations of its specific rotation for sodium light, using a 100 mm. tube, gave as the mean of ten concordant determinations + 36°, whence $[\alpha]_D$ + 38°42′.

The refractive index was determined in a hollow prism of refracting angle 61°25′; the minimum angle of deviation for sodium light was found to be 40°47′, whence $\mu = 1{\cdot}5238$.

Combustions of this hydrocarbon, freshly distilled over metallic sodium, gave the following results:

0·1581 gave 0·510 CO_2 and 0·1615 H_2O. C = 87·9; H = 11·1.
0·2243 „ 0·7269 CO_2 „ 0·2270 H_2O. C = 88·3; H = 11·2.
$C_{20}H_{32}$ requires C = 88·23; H = 11·77 per cent.

The following tabular statement of the properties of the diterpene occurring in the plant and that obtained by destructive distillation of callitrolic acid shows clearly that they are identical:

	B. p.	Rel. dens.	Specific rotation.	Composition.	Refractive index.
Diterpene occurring in resin	260—280°	0·9386	+55°	$C_{20}H_{32}$	1·5215
Diterpene ex-callitrolic acid	270—280	0·9303	+38°42′	$C_{20}H_{32}$	1·5238

The difference in the optical rotation of the two substances is to be accounted for by the production of both dextro- and lævo-forms during the destructive distillation of the callitrolic acid.

Resin of Callitris Verrucosa.

The resin of this plant has been examined in the way already described in detail in the foregoing part of this paper. It contains pinene and a small quantity of a constituent of higher boiling point, of which sufficient could not be obtained for examination from the small amount of resin available. The resin itself is composed of inactive pimaric and callitrolic acids, the former being present in much larger quantity than in the case of the resin of *Callitris quadrivalvis*. The softness of this resin is due to the greater proportion of pinene contained in it which, perhaps, also to some extent affects the rapidity of its solubility in alcohol.

Volatile Resins.

Although it is known that abietic acid is volatile when heated in a vacuum, this substance having been isolated by Kelbe from the distillation products of colophony (*Ber.*, 1880, **13**, 888), and that *d*-pimaric acid can be distilled unchanged in a vacuum (Vesterberg, *loc. cit.*), yet this method has been but little used by investigators for the isolation of resin constituents, the only case of its application (which seems to have been accidental) being the preparation of cannabinol from the resin of Indian hemp by Messrs. Wood, Spivey, and Easterfield (Trans., 1899, **75**, 20). During the course of the present work it was found that distillation of sandarac under reduced pressure was a very con-

venient way of obtaining inactive pimaric acid. The resin was broken into small pieces and placed in a Jena distilling flask having another similar flask attached to its side arm in the usual way. The flasks were then rendered vacuous (10—12 mm. pressure) and the resin heated by a Bunsen burner. At first a little water came over, and the resin melted and began to froth. The frothing was easily controlled by the use of a glass T-piece, inserted between the pump and the flasks, having one arm closed by a piece of rubber tubing and a spring clip, so that the pressure in the flasks could be suddenly increased at will by opening the clip. After a time, the volatile oil began to distil over, the thermometer gradually rising to about 160°. The receiver was changed at this stage, and a fraction up to about 240° collected. This was usually viscous when cold, and was found to be a mixture of pimaric acid and diterpene. The receiver was again changed and a fraction up to 300° collected. This was almost pure pimaric acid, and on redistillation usually gave a large fraction boiling at 260° under 15 mm. pressure which, on solution in alcohol and addition of a little water, could be obtained in a crystalline condition (m. p. 171°). In this process, the callitrolic acid suffers decomposition, and so a large yield of diterpene is obtained in the earlier fractions. This can be purified by shaking the ethereal solution of the fraction with potash to remove pimaric acid, and rectification as already described over metallic sodium.

Among other resins which on distillation under diminished pressure give constituents of constant boiling point are mastic, myrrh, and Indian frankincense. The application of this process could no doubt be extended with great advantage to the investigation of this class of substances, about the chemistry of which so little is known owing to the difficulty of isolating well-defined products from them.

Summary and Conclusions.

Briefly stated, the principal results obtained in the course of the present investigation are as follows.

It is shown that the crude resin consists of a mixture of resin acids and volatile hydrocarbons. The latter have been separated into a diterpene and *d*-pinene.

Two acids have been isolated from sandarac resin. One of these has the composition represented by the formula $C_{20}H_{30}O_2$. It is not identical with abietic acid but is isomeric with Vesterberg's *d*-pimaric acid, and as it differs from the latter in being optically inactive, it is proposed to call it *i-pimaric acid.*

The remaining acid of the resin is probably the chief constituent of Tschirch and Balzer's callitrolic acid, so that the latter name may

conveniently be retained for it. It yields a lactone of the composition $C_{30}H_{46}O_4$, from which it may be inferred that the composition of the acid is represented by the formula $C_{30}H_{48}O_5$. This lactone, although insoluble in all the usual solvents except boiling acetic acid, is dissolved readily by alcoholic solutions of *i*-pimaric acid, and is reprecipitated from such solutions by the addition of alcohol. This phenomenon has already been observed by Johnston (*loc. cit.*), who found that a strong varnish of crude sandarac, made with alcohol, deposited the A *resin* on dilution with more alcohol. This experiment has been repeated, and the A resin of Johnston has been found to be identical with the lactone of callitrolic acid.

The resin of *Callitris verrucosa* has also been examined and found to contain *d*-pinene, and the two resin acids already obtained from common sandarac.

It should be pointed out that in many particulars the observations now recorded do not confirm those of Tschirch and Balzer. The sandaracolic acid of these authors was probably impure *i*-pimaric acid, and could not have given methyl iodide when heated with hydriodic acid, since no constituent of sandarac resin behaves in this way, as has also been shown by Gregor and Bamberger (*Oesterr. Chem. Zeit.*, 1898, **1**, 8), who obtained no methyl iodide when the crude resin was heated in Zeisel's apparatus with hydriodic acid. The formation of acetyl and benzoyl derivatives from sandaracolic acid (impure *i*-pimaric acid) is also inexplicable, except on the assumption that it contained much callitrolic acid, which is hardly probable if, as the authors say, their sandaracolic acid was distinctly crystalline. Tschirch and Balzer further failed to observe the formation of the insoluble lactone when attempts are made to regenerate callitrolic acid from aqueous solutions of its alkali salts by addition of mineral acids. The formulæ now proposed for the acid constituents of sandarac resin also differ considerably from those proposed by these authors.

The experimental results obtained in the course of this work, although not yet sufficiently definite and extensive to enable a constitutional formula to be assigned to *i*-pimaric acid, lend support to the view generally held that the resin acids of the *Coniferæ* are produced by the condensation and oxidation of terpenes; a view to which concrete expression has been given in the constitutional formulæ assigned by Bruylants and by Bischoff and Nastvogel to resin acids of the composition $C_{20}H_{30}O_2$, to which attention has already been drawn in the historical introduction to the present paper.

This investigation has been carried out in the laboratories of the Scientific Department of the Imperial Institute, and I desire to express

my warmest thanks to Professor Dunstan both for the suggestion that I should undertake this work and for the valuable help he has given me during its pursuit.

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CXXIV.—*Gum Tragacanth.*

By CORNELIUS O'SULLIVAN, F.R.S.

I. *Introductory.*

FOR a number of years, I have occupied myself, amongst other things, with a study of the constitution of gum tragacanth, but the investigation is still not so complete as I should have wished it to be. Recently, however, Widtsoe and Tollens (*Ber.*, 1900, **33**, 132) described some of the products of the sulphuric acid hydrolysis of the gum, and this fact leaves me no alternative but to place on record the results I have hitherto obtained, and to indicate the direction in which I am still working.

II. *Earlier Investigations of the Composition of the Gum.*

Of the proximate composition of gum tragacanth, very little seems to be known, and where the character and composition of the proximate constituents are described, it is difficult to resist the conclusion that our knowledge is of little value.

We have to begin with the broad statement that gum tragacanth consists of cellulose, starch, bassorin, a gum like arabin, a little nitrogenous matter, sugar, and ash.

We are not told the nature of the *cellulose*; we have no evidence that the granules contained in the cells are *starch granules*, for although, without doubt, they are coloured blue by iodine, we have no collateral proof in support of the assumption.

Again, I have been unable to ascertain why the cellular matter apparent under the microscope is written down as *cellulose*. It certainly gives a blue coloration with Schultz's reagent, but I can find no further evidence.

Bassorin is a very imperfectly defined substance, and it would indeed be difficult to identify it from the general description given of it (*Gmelin-Kraut*, 1862, **4**, 650).

Of the *soluble gum*, nothing further appears to be recorded than that it resembles *arabin*. The *nitrogenous matter* is simply indicated by the presence of *nitrogen*, and concerning the *sugar* there is no information; but the knowledge of the *ash constituents* is of course satisfactory.

III. *Object of the Work.*

With these facts in my mind, and looking upon gum tragacanth as of the nature of plant sap containing *reserve* matter in an advanced stage of elaboration, it appeared to me—with the light thrown upon the constitution of the gums in general by my work on the gums of the arabin group—that some clearer idea of the constitution of this gum could easily be obtained, and thence of the more immediate materials of reserve matter.

From the general description of bassorin, I was led to believe I should have to deal with some gum acid or acids related to those of the arabin or geddin series in a polymerised state; this, however, was found not to be the case; when the gum was treated with water, the solution was only *slightly acid*, the amount of potash required to render the mucilage neutral being very small, and the solubility thereof being practically unaltered.

IV. *Mode of Procedure.*

When the gum is treated with water, it swells up very considerably, and at least one hundred times its weight of water must be added before any differentiation occurs. The addition of alkalis does not materially alter this, consequently, the usual method of fractionating such materials was not available. When diluted as thus described, however, the so-called cellulose, with jelly-like matter and starch, begins to separate (Kützing, *Philosophische Botanik*, i, 203; H. von Mohl, *Bot. Zeit.*, 1857, 32), and by this means a moderately clear solution, difficult to filter, is obtained. The cellulosic shreds occupy a large space in the liquid, but all attempts to get them to settle satisfactorily met with but indifferent success. Consequently, I determined at the outset to act on the gum with dilute sulphuric acid, to examine the products of the reaction, and then, if possible, to trace each product back to the original material whence it was derived.

The investigation was accordingly carried out in this direction, and yielded interesting results, but as I believe I can describe the nature of the gum without utilising this series of experiments, I shall leave them unrecorded. I may, however, say that it was the knowledge derived from a study of the products of the action of dilute sulphuric acid on the gum—in which I was most materially assisted by Dr. Stern, my assistant at that time—and especially of the products other

than sugars, which enabled me to deal with the problem in the manner described in this paper. The results, so far as the sugars are concerned, will be found in the work of Widtsoe and Tollens (*loc. cit.*), although no indication is there given as to the immediate source of these substances.

I proceeded as follows: When water is added to the gum, the pieces swell up to a more or less transparent jelly, some of them being very nearly transparent, others quite white and opaque, whilst every intermediate stage is also observed.

Examined microscopically, the transparent jelly masses are found to consist of irregular, "blown out" cells, the thin walls being filled with glairy matter; the opaque pieces consist of the same kind of irregular cells, but containing, in addition to the glairy matter in the interior, many granules, apparently starch, which are coloured *blue* by iodine, whilst the intermediate varieties are distinguished by the varying numbers of granules they contain, this number apparently increasing with the opacity.

V. *The Granules.*

Although the granules are distinctive, and are coloured blue by iodine, I thought it desirable to isolate them, and to determine absolutely their identity with starch.

When the gum is submitted to the action of freshly prepared copper-ammonium solution, obtained by treating copper turnings with ammonia in the usual way, nothing is left undissolved but bright, almost transparent granules, which are deposited on the addition of a large bulk of water. On decanting off the copper solution and washing the residue with water, the aqueous filtrate was coloured *brown* by iodine solution, whilst on treatment with dilute hydrochloric acid, a solution was obtained which was coloured *dark purple* by that reagent. On treating the remaining granules with iodine, a coloration not as intensely *blue* as that yielded by starch with the same reagent was observed. It was difficult to obtain the granules in sufficient quantity to admit of a determination whether or no they yielded maltose on treatment with malt extract, but in order to procure some evidence on this point, about 150 grams of the gum were treated with 10 litres of water, after soaking, and allowed to stand for some days. The insoluble portion was then strained out, by means of a linen filter bag, washed with cold water so long as anything dissolved, and then pressed.

Under the microscope, the mass was seen to consist of unaltered granules and shrivelled, cell-wall *débris*. It was treated with boiling water, cooled down to 60—65°, and digested for several hours

with malt extract. A microscopical examination showed that the granules had been dissolved, and on evaporating the filtered solution to a syrup, and digesting this with alcohol of sp. gr. 0·830, a clear solution and an insoluble residue were obtained. The residue was neglected, but the solution, freed from alcohol by distillation and evaporated again to a thick syrup, was taken up by alcohol of sp. gr. 0·820, in which it was completely soluble. After freeing this solution from alcohol, the residue was examined.

The figures yielded by the aqueous solution were as follows: sp. gr. 1·029, α_D^{200*} +8·0°; whence $[\alpha]_D$ +53·1°.

This number approaches that of dextrose so closely as to leave little doubt that we have that substance present. From this observation, I do not, however, think it can be said that we have not starch to deal with, still I feel I am justified in recording the observation that these granules, apparently consisting of starch, yield on treatment with diastase, not maltose, but dextrose.

There is still one more point to which attention should be drawn here, namely, that the cell-walls are dissolved by copper-ammonium solution. Numerous attempts were made to isolate definite entities from this solution, but the results were not satisfactory; hence the use of that reagent in the investigation was discontinued.

VI. *The Cellulosic Substance.*

Since the cell-walls described above did not appear identical in every respect with ordinary cellulose, an examination of the substance seemed desirable. Accordingly, a portion of the original gum was treated with three hundred times its weight of boiling water, digested for some time, and then submitted to filtration through linen bags. The residue left in the bags was repeatedly treated with boiling water, and was finally collected on filter paper, a hot water funnel being employed. The filtered shreds which comprise the whole of the cellular matter are completely soluble in freshly prepared copper-ammonium solution, in which only the granules remained insoluble when the whole gum was treated with the reagent.

Examined microscopically, the cellular mass was found to consist of shreds and *débris*, a portion of which gave a blue colour with zinc chloride solution of iodine, the remainder being coloured reddish-brown; in fact, it was quite obvious that the shreddy mass, although showing in its parts no material differences under the microscope, consist of two or more distinct substances. Besides the cellular shreds, a few hard, well-defined crystals, which are neither sulphate nor carbonate of calcium, are also present, but as they occur in extremely small quantity, I have not examined them further.

* The number gives the length of the tube in which the observation was made, in mm.

The amount of cellular matter present in the gum varied between 1 and 3 per cent. A portion of it was repeatedly extracted with boiling water, dehydrated with strong alcohol, and dried, first in a vacuum and then in a current of dry air at 100° On combustion:

0·322 gave 0·498 CO_2, 0·175 H_2O, and 0·030 ash.

C = 46·51; H = 6·65 per cent. (in substance free from ash). Ash = 10·3 per cent.

These results appear to indicate that the cell-walls do not consist of cellulose proper, however closely they may resemble the oxycelluloses.

The ash contained silica, lime, phosphoric acid, ferric oxide, &c.

Action of Sulphuric Acid on the Cellular Substance.—Some of the cellular matter, purified as described above, was washed, first with a dilute solution of potash, then with dilute hydrochloric acid, and finally with water, till free from chlorine. The jelly thus obtained consisted of shreds, and was digested at 98—99° with a 5 per cent. solution of sulphuric acid for an hour. During the digestion, a marked odour of furfuraldehyde was observed.

At the end of the time stated, the solution was filtered, and the insoluble portion washed with boiling water till free from sulphuric acid. The filtrate was neutralised with baryta water, the precipitated barium sulphate filtered off, and the filtrate concentrated in a vacuum to a syrup; this was then taken up with alcohol of sp. gr. 0·820, in which it was almost entirely soluble. After removal of the alcohol by distillation, the syrup which remained behind yielded, on standing, a crop of microscopic, skiff-shaped crystals of arabinose, such as this sugar yields at times on crystallisation from slighty impure solutions. The crystals were washed with dry methyl alcohol, and dried in a current of dry air at 100°.

1·820 grams, dissolved in water and made up to 100 c.c., gave α_D^{200} +3·5°, whence $[\alpha]_D$ +96·2°.

This figure is low for arabinose, but no lower than I have obtained before under similar conditions. The air-dried crystals lost no weight at 100°.

On recrystallising the preparation from water, crystals with the characteristic terminations of arabinose, as yielded by arabic acid, were obtained. These were washed with methyl alcohol and dried, first in air, and then at 100°.

1·054 grams, dissolved in water and made up to 100 c.c., gave α_D^{200} +2·15°, whence $[\alpha]_D$ +102·0°.

As the low opticity of the sugar at the outset might have been due to the presence of galactose, a portion of the original syrup was treated

with nitric acid of the proper strengh, but no mucic acid was produced; dextrose it might have been, but sufficient material was not at my disposal to determine the point. I consider, however, that most probably the disturbing cause is the substance of low rotatory power which is always produced when arabinose is subjected to the action of sulphuric acid for any length of time.

It is evident, therefore, that the cellular matter, on treatment with sulphuric acid as described, yields practically nothing but arabinose.

The residue from this treatment, insoluble in sulphuric acid, is a jelly-like mass which, under the microscope, appears to consist of a number of shreds with no definite structure, in fact it differs very little in appearance from the original cellular matter. Iodine solution colours some of the shreds blue, others brown, whilst the remainder are unchanged. More of the shreds are coloured blue by zinc chloride solution of iodine than by iodine alone, but some are still only coloured brown; a solution of iodine and sulphuric acid also acts in much the same way, except that a larger proportion of the shreds appear to be coloured blue in this case. A few acicular crystals are still observable.

It is clear from these experiments, therefore, that even after digestion with 5 per cent. sulphuric acid, the residue is not homogeneous, nevertheless a portion of it was dried in a current of dry air at 100°, and subjected to combustion, to enable me to form an idea of the change, if any, which had taken place.

0·336 gave 0·531 CO_2, 0·186 H_2O, and 0·0195 ash.
C = 45·75; H = 6·52 per cent. (in substance free from ash). Ash = 6·15 per cent.

Hence there is a clear indication of a diminution of carbon and hydrogen, which cannot be explained by the elimination of an arabinose group alone; the time at my disposal, however, did not permit of my going more deeply into the question. It may be pointed out, however, that the sugar solution contained a considerable quantity of uncrystallisable matter, a careful examination of which would, very possibly, throw some light on the point. With the object, however, of ascertaining whether or not the above cellulose-like substance contained a fixed cellulose residue, it was repeatedly treated with bromine water and then with ammonia. Under this treatment, it soon became evident that the substance was dissolving gradually, and after about one-third of the original substance had disappeared, the residue was collected, thoroughly washed with boiling water, dehydrated with strong alcohol, and finally dried in a current of dry air at 100°. On combustion of a portion of it,

0·284 gave 0·457 CO_2, 0·1595 H_2O, and 0·008 ash.
C = 45·15; H = 6·42 per cent. (in substance free from ash). Ash = 2·81 per cent.

Here, again, we have a diminution in the carbon and hydrogen, and also, as might be expected, in the ash, with a gradual approach, so far as the carbon and hydrogen are concerned, to the normal composition of cellulose, but since the substance gradually went into solution under the influence of bromine and ammonia, the absence of an unalterable residue of normal cellulose was conclusively proved. Hence it is perfectly clear that the cell walls, seen under the microscope, although they yield many of the reactions of normal cellulose, have so far no ascertainable relationship to it. Whether the substance or substances are converted in the ordinary process of anabolism into true cellulose or not, it is impossible to say, and the series of changes by which such a transformation could be effected is not easy to imagine.

I can only repeat that the cellular matter of gum tragacanth yields many of the reactions of true cellulose and arabinose on treatment with sulphuric acid, but leaves no permanent residue when acted on with bromine and ammonia.

VII. *The Portion of Gum Tragacanth soluble in Water. Sample* I.

On evaporating the aqueous filtrate from the cellulosic shreds, a gelatinous scum forms on the surface of the liquid, and on cooling the solution, after some concentration, a considerable quantity of jelly-like matter falls out; in fact, the solution becomes a jelly if the concentration is carried far enough. An attempt at fractionation was made by skimming off the scum and pressing out the jelly, but no satisfactory results were obtained; hence the solution was concentrated to about one-sixth of its original bulk, and alcohol added gradually in small portions at a time till a "break" was effected, when further addition of alcohol produced a bulky, curdy precipitate, "fraction α." This could be readily separated from the clear, alcoholic mother liquor, which we shall call "fraction β."

VIII. *Fraction* β.

An examination of fraction β was first made. The alcohol was distilled off, and the aqueous solution concentrated in a vacuum to a syrup. On carefully adding alcohol of sp. gr. 0·840 to this syrup, a flocculent precipitate "fraction γ" was thrown out, which was allowed to settle, and on decanting off the clear, supernatant solution and adding more alcohol, a waxy precipitate, similar in appearance to that yielded by gedda gum, was thrown out.

This precipitate was dissolved in a little water, reprecipitated by alcohol of sp. gr. 0·820 in presence of hydrochloric acid, and handled in precisely the same way as described by me in connection with the gedda gums (Trans., 1891, 59, 1032). It was divided into three portions, fractions I, II, III, fraction I being the least soluble. These fractions were freed from hydrochloric acid by repeated precipitation with alcohol, dehydrated with strong alcohol, and finally dried in a current of dry air at 100° under 250 mm. pressure. The optical activity of each fraction was then determined with the following results:

Fraction I. $[\alpha]_D$ −78·0°.
„ II. $[\alpha]_D$ −88·8.
„ III. $[\alpha]_D$ −88·1.

From these it is evident that we have not a homogeneous body to deal with, although the product is not such a mixture as was the case with the gedda gum acids.

A barium salt of fraction II was prepared by neutralising a solution of it at the boiling temperature with clear baryta water, using neutral litmus as indicator. The solution of the barium salt thus prepared was concentrated, precipitated by alcohol, and dehydrated by alcohol of sp. gr. 0·820. On analysis, 0·783 gram of this salt, dried in a current of dry air at 100°, gave 0·037 gram of barium sulphate, BaO = 3·23 per cent.

This figure indicates a molecular weight corresponding to that of a fraction of the gum acids of gedda gum *C* (Trans., 1891, 59, 1073); the rotations, too, of the fractions from the two sources are nearly equal in amount, although opposite in sign. Hence the soluble gum acids of gum tragacanth resemble those of gedda gum, but are lævorotatory instead of dextrotatory.

VIIIA. *Action of Sulphuric Acid on Fraction β purified.*

Fractions II and III of the soluble gum acids mentioned above were mixed, dissolved in water to a 30 per cent. solution, and this was heated in the water-bath to 100°, sufficient diluted sulphuric acid being added to make the mixture contain 3 per cent. of that acid. The digestion was continued for 15 minutes, and, after cooling, the acid was neutralised with clear baryta water. The whole was then concentrated in a vacuum to a syrup, because the barium sulphate could not be satisfactorily removed by filtration. This syrup was precipitated by excess of alcohol of sp. gr. 0·820, and the clear alcoholic solution containing the sugar or sugars was freed from alcohol by distillation, concentrated in a vacuum to a syrup, which was then

taken up by as little dry methyl alcohol as possible; a small amount of barium salt remained insoluble.

The clear methyl alcoholic solution, on standing, yielded stellate groups of crystals, with the terminations and general characteristics of arabinose. These were collected, washed with methyl alcohol, and their optical activity determined. It was found to be $[\alpha]_D$ +90·8°. As, however, this number was far too low for arabinose, the crystals were redissolved in methyl alcohol, a little insoluble matter filtered off, and the solution again allowed to crystallise. Three crops of crystals were collected, namely, *a*, *b*, and *c*, and the optical activity of each was determined, with the following results:

a $[\alpha]_D$ +102°.
b $[\alpha]_D$ +104.
c $[\alpha]_D$ +106.

These numbers clearly agree with those accepted for arabinose, and although the crystals have not absolutely the same form as that assumed by arabinose obtained from arabic acid, there can be no doubt about their identity with that substance. The amount of arabinose, including the uncrystallisable matter in the mother liquors, yielded by the gum acid varied between 73·0 and 76·7 per cent. of the dry material taken.

When the percentage of arabinose thrown out in arriving at this stage is considered, the high molecular weight attributed to the original soluble gum acid is amply confirmed.

The precipitate thrown down by alcohol, from which the sugar solution was separated by decantation, was treated with a little water, and sufficient sulphuric acid added to convert nearly all the barium present into sulphate. Alcohol was then added until the solution "broke." In this way, the barium sulphate easily falls out and can be separated, whilst the partially degraded gum acid is retained in the dilute alcoholic solution. This can be precipitated by the addition of strong alcohol, and may be easily freed from excess of sulphuric acid by redissolving in water and reprecipitating with alcohol several times.

After freeing from sulphuric acid, the degraded gum acids were divided into two fractions by means of alcohol. Each fraction was converted into a powder by means of strong alcohol. Barium salts were also made by neutralising a portion of each with clear baryta water, and precipitating the concentrated solutions with strong alcohol, and these were dried in the usual way.

An examination of the free acid and barium salt of each fraction was made, with the following results:

Free acid. Most soluble portion gave $[\alpha]_D$ +33·5°, and the barium salt thereof BaO = 10 per cent.

Free acid. Least soluble portion gave $[\alpha]_D$ +33·2°, and the barium salt thereof BaO = 8·8 per cent.

In each of these instances, the substance was dried in a current of dry air at 100°.

If these factors are compared with those obtained for tri- and di-galactangeddic acids (Trans., 1891, 59, 156—157), an almost exact agreement is observed, hence these degraded gum acids are a mixture of the tri- and di-galactangeddic acids.

In further confirmation of the galactan nature of these degraded gum acids, a determination was made of the amount of mucic acid formed from them by treatment with nitric acid in the usual way. Seventy to eighty per cent. of mucic acid was thus obtained, and this result confirms the identity of these degraded acids with those of the geddic series. As was naturally to be expected, on further treating these acids with sulphuric acid, galactose and a further degraded acid, corresponding to, if not exactly identical with, geddic acid were obtained. In order to determine whether or not other samples of gum tragacanth would yield like results, a fresh sample of the gum from a different source was examined.

IX. *Portion of the Gum soluble in Water. Sample II.*

A. *Examination of Fraction corresponding to β-Fraction.*

On treating the second sample of gum tragacanth in precisely the same way as described for the first, a product was obtained corresponding to β-fraction, which yielded fractions with opticities $[\alpha]_D$ −96° to $[\alpha]_D$ −115°; these gave barium salts which contained from 4 to 5·4 per cent. BaO, the evidence, curiously enough, being that the neutralising power for barium increases with rising rotatory power. When these results are compared with those obtained for the similar acids yielded by sample I, it becomes evident that we are dealing with members of the same series.

Sample I.	Free acid	$[\alpha]_D$	−88°;	barium salt	3·23	per cent.	BaO.
„ II.	„	$[\alpha]_D$	−96;	„	4·0	„	„
„ II.	„	$[\alpha]_D$	−115;	„	5·4	„	„

It is clear, therefore, that although the gum acids belong to the same series, the number of arabinose yielding groups is less in the more optically active acids than in those producing a smaller rotation.

IXB. *Action of Sulphuric Acid on β-Fraction. Sample II.*

We have now to decide whether or not this is the only difference between the gum acids. To determine it, fractions of opticity between

$[\alpha]_D$ −95° and $[\alpha]_D$ −100°, neutralising about 4 per cent. barium, were mixed and digested with 3 per cent. sulphuric acid for 30 minutes. The products were separated as usual, and 72·5 per cent. of sugar of $[\alpha]_D$ +100° was obtained. This was recrystallised from methyl alcohol, and several crops were separated which possessed the characteristic terminations of arabinose and yielded the following factors:

$$[\alpha]_D +101—104°. \quad K\ 101—105.$$

These figures conclusively prove that the sugar is arabinose. Much non-crystallisable matter possessing a low opticity was present in this as in the first case, but whether this is produced by the action of sulphuric acid on arabinose, or represents a sugar which, like dextrose, crystallises with difficulty in presence of contaminating matter, I am unable to say.

Amongst some of the products of the reaction, galactose is present without doubt, for on treating this uncrystallisable matter with nitric acid, mucic acid is produced.

X. *The Degraded Gum Acids from Sample II.*

Using the method of purification and fractionation already mentioned, products were obtained having opticities varying between $[\alpha]_D$ +34° and $[\alpha]_D$ +40·6°, and yielding neutral barium salts containing 10—11·8 per cent. of BaO. These figures agree almost absolutely with those obtained when the first sample of the gum employed was subjected to similar treatment, notwithstanding the fact that the original acids acted on by sulphuric acid varied considerably in optical activity.

I may here indicate that these degraded acids are necessarily mixtures, the more highly dextrorotatory portions being those from which a portion of the constituent yielding galactose has been removed, whilst those of lower opticity have either lost less of this constituent, or only part or the whole of that yielding arabinose.

XI. *Further Hydrolysis of the Degraded Acids.*

The fractions having $[\alpha]_D$ +34° to +40·6° just mentioned were mixed, dissolved in water to a 30 per cent. solution, and digested at about 98° for 2 hours with 4 per cent. sulphuric acid. Clear baryta water was added to neutralise the cooled liquid, and then alcohol of sp. gr. 0·850 so long as a precipitate was formed. This consisted of the barium salt of the degraded acids, some sugar, and barium sulphate. The clear alcoholic solution containing the greater part of the sugar or sugars was decanted off, and the precipitate further freed from sugar by digesting with alcohol of sp. gr. 0·870, redissolving in a little

water without separating the barium sulphate, and reprecipitating several times with alcohol of the strength mentioned.

The alcoholic solutions thus obtained were mixed, the alcohol distilled off, and the residual solution concentrated in a vacuum to a syrup. On examination, the solid matter in this was found to have an optical activity $[\alpha]_D$ +60—65°, and to contain barium salts of gum acids. Consequently the whole of the syrup was digested for some time with alcohol of sp. gr. 0·820 in a flask with a reflux condenser. Much gummy matter remained insoluble, and, on cooling, more was precipitated, leaving the alcoholic solution clear. When this solution was again freed from alcohol and concentrated in a vacuum, a syrup was obtained which crystallised on standing. After a few recrystallisations, the substance had a crystalline form similar to that exhibited by galactose under certain conditions.

On examination, the crystals yielded the following results:

$$[\alpha]_D +80—83°. \quad K = 93—95°.$$

and on treating them with nitric acid under the most favourable conditions, 72—75 per cent. of mucic acid was obtained. Hence the sugar is undoubtedly *galactose*.

Returning now to the barium salt, partially freed from the sugar as just described. It was treated with the least possible quantity of water, and an attempt unsuccessfully made to separate the barium sulphate by filtration; it was not possible to obtain a clear filtrate, consequently sulphuric acid was carefully added until the barium present was completely precipitated, and then alcohol until a "break" was effected, when the barium sulphate with a little gum acid separated out, leaving the alcoholic solution clear. This was decanted off; it contained the greater part of the degraded gum acid. Treatment with alcohol of sp. gr. 0·820 enabled me to separate this into two fractions. *a*, a less soluble one, and *b*, one more soluble; these were dried in the usual way and the optical activity of each determined:

a gave $[\alpha]_D$ +93·8°.
b „ $[\alpha]_D$ +94·1°.

A barium salt of each was prepared, that of:

a yielded BaO = 18·1 per cent.
b „ 17·6 „

In another series of experiments in which the acids with opticities between $[\alpha]_D$ +34° and 40° were acted upon with 4 per cent. sulphuric acid for 4 hours, degraded acids were obtained in precisely the same way as described, of which the optical activity was somewhat higher, namely, $[\alpha]_D$ +109·7—109·5°, but the barium salts of these yielded practically the same numbers, namely, BaO = 18·6—18·03 per cent.

To enable me to form some notion of the composition of these substances, one of the apparently purest barium salts, dried in dry air at 100° under 275 mm. pressure, was burned with the following results:

0·474 gave 0·573 CO_2, 0·184 H_2O, and 0·113 $BaCO_3$. C = 34·41; H = 4·32; BaO = 18·51.

$C_{23}H_{36}O_{21},BaO$ requires C = 34·45; H = 4·49; BaO = 19·10 per cent.

I have attributed (Trans., 1891, 59, 1054) the formula $C_{23}H_{38}O_{22}$ to geddic acid of $[\alpha]_D$ +71° and $C_{23}H_{38}O_{22}BaO$ to its barium salt. The latter formula requires C = 33·70; H = 4·64; BaO = 18·58 per cent.

On comparing these results, we observe a broad agreement between them, but one not sufficiently close as to enable us to state that the degraded acids from both sources are identical, although it can hardly be doubted that there is a close relationship. The composition of the two acids is no doubt the same, namely, $C_{23}H_{38}O_{22}$, but geddic acid has α_D +71°, whilst the acid under consideration has α_D +100° to 109°, and the barium salts are different, as is shown by the analyses.

In dealing with non-crystallisable substances of this kind, and taking cognisance of the fact that they are exceedingly difficult to dry, I do not wish to draw more inferences than the analytical numbers warrant. But, I may say these have not been based on one set of experiments, but on many. Hence, I feel justified in concluding that the degraded acid of tragacanth, if not absolutely identical with geddic acid, very closely resembles it, and, on comparing the products obtained from both the original undegraded acids after being acted upon by sulphuric acid for 10 to 15 minutes, I feel convinced that the partially degraded acids obtained in each case are very closely related, if not identical. They both have the same optical activity, and their barium salts yield the same amount of baryta, as has been shown above.

It is sufficiently clear that the primary acids of gum tragacanth are not identical with those obtained from gedda gum, although they have many properties in common, the chief differences being that the former acids are lævorotatory, whilst the latter are dextrorotatory, and, unlike the gedda gum acids, do not yield *arabinon* as a product of their partial hydrolysis with sulphuric acid.

Possibly, this occurrence of arabinon-yielding acids may have something to do with the differences in the direction of the rotation, especially as the products after the elimination of the arabinon groups agree so closely in optical properties and neutralising power.

It is thus evident that the *acids of gum tragacanth, soluble in dilute alcohol* are polyarabinon-trigalactan-geddic acids, namely, $xC_{10}H_{16}O_8,3C_{12}H_{20}O_{10},C_{23}H_{38}O_{22}$, with the differences indicated above and by this formula.

One of the fractions of the soluble gum acid under consideration, namely, that with $[\alpha]_D$ $-88°$ and containing 3·23 per cent. BaO in the barium salt, is probably represented by the formula:

$$11C_{10}H_{16}O_8.3C_{12}H_{20}O_{10},C_{23}H_{36}O_{21},BaO.$$

This requires 3·29 per cent. BaO, and should yield on partial hydrolysis 71·7 per cent. of arabinose. It has been shown above that between 72 and 76 per cent. of moderately pure arabinose was obtained from the mixed gum acids.

From these facts, it appears clear to me that the constitution of the soluble gum acid of gum tragacanth has, broadly, been sufficiently well established and indicated.

The Nitrogenous Matter.

Of this, I cannot at present say more than that it is less soluble in alcohol than the gum acids just described, in fact, it is fraction γ, mentioned on page 1170; that, when once precipitated and dried, it does not again give a clear solution in water, whilst it is soluble, with a slight brown colour, in potash, and that it does not give the proteid reactions given by the nitrogenous substance from gedda gum (Trans., 1891, 59, 1061).

XII. *Fraction α. The Jelly-like Portion. "Bassorin."*

It has been pointed out in the earlier portion of this paper that the clear filtrate, obtained in the process of removing the cellulose-like shreds from the product of the digestion of gum tragacanth with a large bulk of water, yielded on evaporation a gelatinous scum and a jelly-like deposit, and that the solution, when brought to this state of concentration, yields the bulky precipitate with dilute alcohol which was mentioned when the elimination of the soluble gum acids, fraction β, was described.

This precipitate was repeatedly washed with dilute alcohol, dissolved in the least possible quantity of water, acidified with hydrochloric acid, and placed upon a dialyser to free it from salts of calcium, magnesium, &c. When the solution on the dialyser was free from hydrochloric acid, dilute alcohol of sp. gr. 0·870 was added to it; a white, curdy precipitate was thrown out, which, on decanting off the supernatant liquid and adding stronger alcohol, became shred-like. This was well washed with alcohol of sp. gr. 0·850, and then dehydrated by alcohol of sp. gr. 0·825, when it could readily be rubbed down to a powder. It is undoubtedly the substance known as *bassorin*.

This preparation, dried until constant in a current of dry air at 100°, gave $[\alpha]_D$ +98°.

I do not give the analytical numbers, because up to this point I have no criterion of the purity of the substance. It may, however, be here pointed out that the opticity of the gum acids soluble in alcohol of sp. gr. 0·870 is almost identical with the above number, although opposite in sign.

A barium salt of the preparation was made by neutralising an aqueous solution thereof with clear baryta water. While doing this, it was noticed that at the point where the baryta water dropped into the solution, and, consequently, where the reagent was in excess, a lemon-yellow colour was developed. By cautious addition of the reagent, however, a neutral solution was obtained without the production of much colour, and this, on addition of alcohol, yielded a curdy precipitate, which, after being washed with dilute alcohol and dried in a current of dry air at 100°, contained BaO = 9·2 per cent.

XIIA. *Conversion of Bassorin into α- and β-Tragacanthan-xylan-bassoric Acids.*

When an attempt was made to dissolve the above barium salt for the estimation of the barium, a portion was found to be insoluble; hence, it seemed as if some change had taken place, presumably under the influence of the alkali employed.

Numerous attempts were made to purify the original bassorin by partial precipitation with alcohol, but with no great success, consequently the whole preparation was converted into a barium salt by treatment with baryta water. After this salt had been dried in a vacuum over sulphuric acid, and finally in a current of dry air at 100°, it was observed that a part was *insoluble* in water, as already mentioned. The insoluble portion admitted of being easily filtered off. The filtrate was submitted to dialysis in presence of hydrochloric acid until free from barium. To the solution, alcohol was added, and the precipitate, after redissolving and reprecipitating with alcohol several times until all the hydrochloric acid had been removed, was strained out, pressed, dehydrated, dried in a vacuum over sulphuric acid, and finally in a current of dry air at 100°.

0·971 gram, dissolved in water and made up to 50 c.c., gave a solution of sp. gr. 1·0083 and an opticity α_D^{200} +2°5′, whence

$$[\alpha]_D +128°. \quad D = 4·27.$$

It will be noticed that the $[\alpha]_D$ is much higher than that of the original substance, and the divisor much greater than that of any known carbohydrate. Further, it is obvious that we have in no way to deal with the original material.

On attempting to prepare a barium salt of this substance by neutralising its aqueous solution with clear baryta water, the addition being made drop by drop, a gelatinous precipitate was immediately thrown out. This precipitate, formed in as neutral a solution as possible, was collected and washed, first with water, then with dilute alcohol, and finally dehydrated and dried as usual. On analysis:

0·448 gave $BaSO_4 = 0·116$. $BaO = 17·0$ per cent., a result which confirms the conclusions arrived at from the $[\alpha]_D$ and D.

As has been mentioned previously, the neutralisation of the original solution of bassorin with clear baryta water gave rise to no precipitate of any kind, whereas the neutralised solution yielded on precipitation with alcohol a substance which, after drying, was not again entirely soluble in water. The *portion* of the neutralised precipitate insoluble in water was also insoluble in hydrochloric acid, but was soluble in potash or ammonia.

From these facts, it is evident that the substance known as bassorin is not a stable compound, but undergoes some change under the influence of the alkali employed in the preparation of one of its salts. What the nature of this change is, I do not propose to discuss at present; it is sufficient to say that when an *excess* of milk of lime or baryta water is added to a strong solution of bassorin in water, a dense, curdy, light lemon-yellow precipitate is thrown down, which can be collected, washed with alcohol, dehydrated, and dried at 100° without developing a more intense coloration. On treating the dry mass with an excess of dilute hydrochloric acid, much carbon dioxide is evolved, and a large, semi-curdy portion remains insoluble; this can be easily filtered off, the filtrate being perfectly clear.

The insoluble portion admitted of being washed with cold water, and dehydrated and dried as usual by treatment with strong alcohol. This may be called *fraction B.*

Addition of alcohol to the clear acid filtrate yielded a curdy precipitate called *fraction A.* We shall deal with the latter first.

Fraction A.

The white, curdy precipitate was washed free from hydrochloric acid by dilute alcohol, and was pressed and dried. A small portion of this substance was found to be insoluble in water. This was collected, and alcohol added to the filtrate so long as a precipitate was produced. On drying as usual, this yielded the following results on analysis:

0·83 gram, dissolved in water and made up to 50 c.c., gave a solution of sp. gr. 1·00696 and α_D^{100} +4·5°, whence

$[\alpha]_D$ +135. D = 4·19.

It will be observed that this opticity is still higher than that of the substance with which I started. Is the substance even now homogeneous?

To ascertain this, an aqueous solution of the acid was treated with sufficient clear lime water to precipitate about half the solid matter present. A bulky precipitate of calcium salt was thrown out, which was easily filtered, and could be readily washed with water and dilute alcohol; this was pressed and dried as before. We call this portion *fraction* A_1.

To the filtrate, hydrochloric acid in excess was added, and then alcohol so long as a precipitate was formed. This was collected on a filter, washed with dilute alcohol until free from chlorine, and then dried. We call it *fraction* A_2.

Both fractions were redissolved in water containing hydrochloric acid, then reprecipitated with alcohol, and washed free from the acid. They were again redissolved and reprecipitated several times, and analyses of each made, with the following results.

Fraction A_1.—1·288 grams (dried in dry air at 100° under 300 mm. pressure), dissolved in water and made up to 50 c.c., gave a solution of sp. gr. 1·01062 and α_D^{200} +7·14°, whence $[\alpha]_D$ +138·6° and D 4·12.

Fraction A_2.—1·700 grams, dissolved in water and made up to 50 c.c. gave a solution of sp. gr. 1·01404 and α_D^{200} +9·4°, whence $[\alpha]_D$ +138·2° and D 4·13.

These results justified me in considering that I had a pure substance to deal with, and accordingly I was able to proceed to its analysis.

Combustions of fractions A_1 and A_2, dried in dry air at 100° and 300 mm. pressure, were made, with the following results:

Fraction A_1.—0·341 gave 0·537 CO_2, 0·169 H_2O, and 0·003 ash.
C = 43·43; H = 5·56; ash = 0·80 per cent.

Fraction A_2.—0·338 gave 0·530 CO_2, 0·166 H_2O, and 0·004 ash.
C = 43·41; H = 5·52; ash = 1·20 per cent.

The ash in both cases was mainly calcium carbonate.

These numbers confirm the conclusions arrived at from the opticities and D, namely, that the substance is homogeneous.

The empirical formula calculated from these numbers is $C_{24}H_{36}O_{21}$, which requires:

C = 43·63; H = 5·46 per cent.

Barium Salt.—A portion of the acid used in the foregoing analysis was dissolved in water, neutralised at the boiling point with ammonia, neutral litmus paper being used as indicator, and barium chloride solution added so long as a precipitate was formed. The precipitate so

obtained was collected and washed with cold water until free from chlorine.* The barium salt so prepared can be easily dried in the usual way, and rubbed down to a fine powder. On analysis:

0·388, dried in dry air at 100°, gave $BaCO_3$ 0·096. BaO = 19·21.
$C_{24}H_{34}O_{20}$,BaO requires BaO = 19·24 per cent.

Determinations as $BaSO_4$ yielded the same results.

Calcium Salt.—This salt is prepared similarly to the above, and behaves in like manner, but its solubility in water is slightly greater.

0·326, dried in dry air at 100°, gave $CaCO_3$ 0·048. CaO = 8·24.
$C_{24}H_{34}O_{20}$,CaO requires CaO = 8·02 per cent.

Further details concerning these products need not now be given, as I propose to treat the subject more fully in a future paper.

Silver Salt.—An attempt was made to prepare the silver salt of the acid, but the task was beset with many difficulties. About 0·5 gram of the acid was dissolved in water, neutralised with ammonia, and the solution made up to about 45 c.c. On adding ordinary silver nitrate solution to this, the whole was converted into a transparent jelly of sufficient density to admit of the beaker being inverted without disturbing its contents. One hundred c.c. of water were added, and the mixture well stirred and thrown upon a filter, the operation being conducted in a room lighted by ruby light. Much of the liquid passed through, but it was difficult to free the precipitate entirely from its mother liquor. This end, however, was to some extent achieved by pressing the gelatinous mass between folds of filter paper, but on attempting to wash the fairly dry substance with water, it again swelled up, and the above process of filtration and drying had to be repeated. On drying in a vacuum over sulphuric acid in the dark, the salt became brown, and when an attempt was made to dry it in a current of dry air at 100°, it blackened completely.

Under these circumstances, it seemed hardly worth while to estimate the silver in the preparation, but in the hope that an analysis might lend some support to the conclusions indicated by the previous experiments, a portion of the salt, dried in a vacuum over sulphuric acid (not, however, until constant, owing to slow decomposition of the salt) was analysed, with the following results:

0·372 gave 0·11 AgCl. Ag = 22·2.
$C_{24}H_{34}O_{20}$,Ag_2O requires Ag = 24·77 per cent.

* The barium salt is sufficiently soluble in cold water to give a precipitate with silver nitrate, that is, the silver salt of the acid is less soluble than the barium salt, consequently the absence of chlorine must be proved by silver nitrate in presence of nitric acid.

This result is, considering the circumstances, sufficiently close to support the conclusions based on previous experiments.

To the gum acid giving rise to these salts, the name *α-tragacanthan-xylan-bassoric acid* may be given, for reasons which may simply be indicated here.

Hydrolysis of α-Tragacanthan-xylan-bassoric Acid.

When a 20 per cent. solution of the acid is digested for 20 minutes at the temperature of a boiling water-bath with a 5 per cent. solution of sulphuric acid, a sugar is obtained on the one hand which proves to be a pentose having the opticity $[\alpha]_D$ −30° or thereabouts. This is a new sugar which I propose to name "*tragacanthose*" (it may be *l*-xylose, but I have not sufficient of the substance to enable me to decide the point at present); on the other, a new acid is produced the barium salt of which was found on analysis to contain 22·5 per cent. BaO. $C_{19}H_{26}O_{16}BaO$ requires BaO = 23·07 per cent., and the acid from this salt on combustion gave numbers corresponding with those required by the formula $C_{19}H_{28}O_{17}$.

The action of sulphuric acid upon α-tragacanthan-xylan-bassoric acid—$[\alpha]_D$ +135°—is represented by the following equation:

$$C_{24}H_{36}O_{21} + H_2O = \underset{\substack{\textit{Tragacanthose}\\ \text{or } l\text{-xylose.}}}{C_5H_{10}O_5} + \underset{\textit{Xylan-bassoric acid.}}{C_{19}H_{28}O_{17}}$$

The opticity of the new gum acid in neutral solution (potassium salt) was found to be $[\alpha]_D$ +200° or thereabouts. This acid is only slightly soluble in cold water, and its barium and calcium salts are almost insoluble.

On acting upon *xylan-bassoric acid* still further with 5 per cent. sulphuric acid in the same way as on the original substance, another sugar, xylose, was eliminated and another new acid, namely, *bassoric acid*, was produced. The action of sulphuric acid is represented by the following equation:

$$C_{19}H_{28}O_{17} + H_2O = \underset{\text{Xylose.}}{C_5H_{10}O_5} + \underset{\text{Bassoric acid.}}{C_{14}H_{20}O_{13}}$$

The sugar produced was proved to be xylose by its crystalline form, K, optical activity $[\alpha]_D$ +21° (it has a high temporary activity), and by the depression of the freezing point of its solutions.

Bassoric acid is only very slightly soluble in cold water, it gelatinises on treatment with boiling water and separates from this jelly, on cooling, in much the same way as inulin does from its solutions. The optical activity of the acid in alkaline solutions was $[\alpha]_D$ +255°, and the neutral barium salt contained BaO = 28 to 29 per cent.

$C_{14}H_{18}O_{12}BaO$ requires BaO = 28·8 per cent. This salt is almost insoluble in water.

I shall not describe this final acid further on this occasion, but I may point out that the composition seems to indicate a combination of two hexans with C_2O_3.

$$\left.\begin{matrix}C_6H_{10}O_5\\C_6H_{10}O_5\end{matrix}\right\} C_2O_3 = C_{14}H_{20}O_{13}.$$

I have sufficient acid to determine this point and other things connected therewith definitely, and the work is in hand.

Fraction B.

The crumb-like substance, left insoluble in hydrochlorie acid when the dried precipitate obtained with milk of lime was treated with that reagent (p. 1179), was washed free from hydrochloric acid with cold water, rubbed down to a powder with alcohol of sp. gr. 0·820, dried in a vacuum over sulphuric acid, and then in dry air at 100°.

0·972 gram so dried, dissolved in the least possible quantity of potash, and the solution made up to 50 c.c., gave α_D^{200} +6·0°, whence $[\alpha]_D$ +154°.

Barium Salt.—A portion of the acid was converted into barium salt by precipitating the neutral potassium salt solution with barium chloride, filtering off the precipitate, washing free from chlorine, and drying it with alcohol, then in a vacuum over sulphuric acid, and finally in dry air at 100°.

0·378 gram of the salt thus dried was treated with excess of dilute hydrochloric acid in the cold for 24 hours, and the insoluble residue filtered off and washed free from hydrochloric acid. The barium in the filtrate was precipitated in the usual way as sulphate. It amounted to 0·107 gram $BaSO_4$, hence BaO = 18·6 per cent.

The percentage of BaO agrees sufficiently closely with that yielded by the barium salt of fraction A, to indicate that we have a substance of the same composition to deal with, but there is no evidence, so far, that the material is homogeneous.

I converted the whole of the portion of $[\alpha]_D$ +154° into barium salt. It may be pointed out that unless the solution of the ammonium or potassium salt is not moderately concentrated, the barium salt is not thrown out in an easily filterable condition on the addition of the barium chloride.

The barium from the salt was extracted with hydrochloric acid as already described, and the free insoluble acid was divided into two fractions by dissolving it in the least possible quantity of ammonia and partially precipitating the solution with barium chloride. The first precipitate, which may be called B_1, after continued stirring was

filtered off, and a second, B_2, precipitate was obtained from the filtrate by adding more barium chloride solution.

Both fractions were dried and freed from barium by treatment with hydrochloric acid as described already.

Fraction B_1, 0·766 gram (dried in a vacuum over sulphuric acid and in dry air at 100°), dissolved in the least possible quantity of dilute potash, and the solution made up to 50 c.c. gave α_D^{200} +5·0°, whence $[\alpha]_D$ +163·2°.

Fraction B_2. The fraction from the second precipitate with barium chloride was treated and examined in the same way.

0·684 gram in 50 c.c dilute potash solution, gave α_D^{200} +4·5°, whence $[\alpha]_D$ +164·5°.

These numbers are in sufficient agreement to warrant the conclusion that the substance dealt with is practically homogeneous. On combustion of a portion of each of the fractions, the following results were obtained.

Fraction B_1.

0·3525 gave 0·5565 CO_2, 0·1795 H_2O, and 0·0020 ash.

Fraction B_2.

0·3715 gave 0·5880 CO_2, 0·1870 H_2O, and 0·0005 ash.

	B_1.	B_2.	
C.....	43·30 per cent.	43·24 per cent.	Calculated on substance free from ash.
H....	5·68 „	5·59 „	
Ash..	0·57 „	0·17 „	

These numbers agree sufficiently well among themselves, and if they be compared with those obtained for α-tragacanthan-xylan-bassoric acid, the agreement is so close as to warrant the conclusion that the two acids are isomeric. I shall call this acid *β-tragacanthan-xylan-bassoric acid.*

This conclusion was confirmed by an examination of the products of the sulphuric acid, hydrolysis of the β-acid, the lævorotatory sugar, xylan, the intermediate acid $[\alpha]_D$ +200° (barium salt of which contains 22·46 per cent. BaO), and the final acid with $[\alpha]_D$ +255° and a barium salt containing 28·8 per cent. BaO being obtained.

So far, these two acids are described with sufficient distinctiveness to enable anyone to recognise either of them, and in this position I leave them for the present.

I hope in the immediate future to describe *bassorin* itself more accurately, to indicate the reactions by which it is connected with α- and β-tragancanthan-xylan-bassoric acids, and to describe more closely the lævorotatory pentose, which is the first product of their hydrolysis

by sulphuric acid. There can be no doubt that xylose is the second sugar eliminated. Of this, however, I may have something further to record later on.

Both xylan-bassoric and bassoric acids were eliminated from the products of the action of sulphuric acid on the undifferentiated gum, but it was difficult to prepare pure substances, as mixtures of tragacanthan-xylan-bassoric acids with these acids existed amongst the products.

I have to thank my assistants, Dr. A. L. Stern and Mr. J. A Walker, M.A. (Oxon.), for the helpful assistance they have given me in carrying out the work of which, I in justice must say, this paper is only a brief summary, but which I hope to amplify in the immediate future, more especially in dealing with the cellulosic residue, the nitrogenous constituent, and bassorin.

CXXV.—*Condensation of Phenols with Esters of the Acetylene Series. Part VI.*

By Siegfried Ruhemann and Ernest Wragg, B.A.

Previous researches led to the result that ethyl acetylenedicarboxylate and ethyl chlorofumarate yield the same esters on treatment with the sodium phenolates, and that the acids formed from them on hydrolysis readily condense to derivatives of 1 : 4-benzopyrone under the influence of concentrated sulphuric acid. As has also been shown, the acids obtained from the products of the interaction of the sodium phenolates with ethyl phenylpropiolate cannot be thus transformed into flavone and its homologues, but on distillation lose carbon dioxide, yielding phenoxystyrene and its homologues, and on treatment with sulphuric acid decompose into carbon dioxide, acetophenone, and the corresponding phenols.

Similar is the behaviour of the substances produced from eugenol and *m*-xylenol, which is described in this paper. Although we have not been able to obtain the benzopyrone compound from eugenoxyfumaric acid, yet xylenoxyfumaric acid can readily be condensed to dimethylbenzopyronecarboxylic acid. *β-m*-Xylenoxycinnamic acid, on the other hand, is completely decomposed by sulphuric acid.

The fact that the aryl ethers of *β*-hydroxycinnamic acid are not transformed into benzopyrone derivatives induced us to ascertain whether this reaction is prevented from taking place only by the presence of the phenyl group, or whether hydrocarbon radicles in general

have this effect. For this purpose, we have studied ethyl β-phenoxycrotonate, which is formed by the action of sodium phenolate on ethyl β-chlorocrotonate, and have found that the corresponding acid does not yield a benzopyrone compound, but undergoes changes similar to those observed in the case of the aryl ethers of β-hydroxycinnamic acid. On heating, it loses carbon dioxide and forms β-phenoxypropylene, thus:

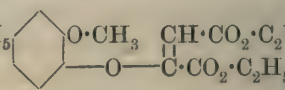
$$CH_3\cdot C(O\cdot C_6H_5):CH\cdot CO_2H = CO_2 + CH_3\cdot C(O\cdot C_6H_5):CH_2,$$

whilst under the influence of sulphuric acid it suffers the following decomposition:

$$CH_3\cdot C(O\cdot C_6H_5):CH\cdot CO_2H + H_2O = CO_2 + CH_3\cdot CO\cdot CH_3 + C_6H_5\cdot OH.$$

With the view of testing whether the difference in the behaviour of the aryl ethers of β-hydroxycinnamic and β-hydroxycrotonic acids from that of the ethers of hydroxyfumaric acid is caused by the configuration of the unsaturated acids, we have subjected β-chloro*iso*crotonic acid, instead of its stereoisomeride, to the action of sodium phenolate. We find, however, that the same compound is formed as when ethyl β-chlorocrotonate is used. This result may be explained by the assumption that the formation of ethyl β-phenoxycrotonate is preceded by the addition of sodium phenolate to the chlorocrotonic esters, accompanied by the transformation of ethyl β-chlorocrotonate into ethyl β-*iso*chlorocrotonate. The resulting substance would thus have the configuration $\begin{matrix} CH_3\cdot C\cdot O\cdot C_6H_5 \\ \| \\ CO_2Et\cdot C\cdot H \end{matrix}$, which on account of the axial position of phenoxyl to the ester group could not yield a benzopyrone compound.

Experimental.

Ethyl Eugenoxyfumarate,  .

The union of eugenol with ethyl chlorofumarate takes place when the unsaturated ester (1 mol.) is gradually added to a solution of sodium (1 at.) in an excess of the phenol. The dark, viscous product is heated for a short time, and, after standing for several hours, treated as in the former cases. The ester is a yellowish oil which boils at 231—232° under 14 mm. pressure; it possesses an aromatic odour, and at 21°/21° has the density 1·1256. On analysis:

0·2030 gave 0·4822 CO_2 and 0·1247 H_2O. C = 64·73; H = 6·82.
$C_{18}H_{22}O_6$ requires C = 64·67; H = 6·58 per cent.

Eugenoxyfumaric Acid, $C_3^{[1]}H_5(O\cdot C^{[3]}H_3)C_6H_3\cdot O^{[4]}\cdot C(CO_2H):CH\cdot CO_2H$.—The potassium salt of the acid separates as a crystalline solid on boil-

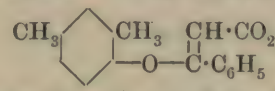
ing the ester with alcoholic potash for 2—3 hours. After the product has been freed from alcohol by distillation on the water-bath, water is added to the residue, and the solution treated with an excess of dilute sulphuric acid, when the organic acid separates as an oil. This is prevented from solidifying on account of the presence of eugenol, which is formed along with eugenoxyfumaric acid on hydrolysis of the ester. In order to remove the phenol, the ethereal solution of the oil is shaken with sodium carbonate, and an excess of dilute sulphuric acid added to the aqueous layer. The organic acid which separates is best extracted with ether, and, after complete evaporation of the latter, remains as a yellow solid, which is very soluble in ether or alcohol. It readily dissolves in boiling water, and, on cooling, crystallises in yellowish plates which melt and decompose at 172—173°. On analysis:

0·2142 gave 0·4755 CO_2 and 0·0980 H_2O. C = 60·54; H = 5·08.
$C_{14}H_{14}O_6$ requires C = 60·43; H = 5·03 per cent.

Eugenoxyfumaric acid dissolves in concentrated sulphuric acid, forming a dark red solution. After standing overnight, it is gradually poured into cold water, when a brownish, gelatinous precipitate is produced, which we have been unable to obtain in a crystalline form, and therefore have not further examined.

Action of the Sodium Derivative of m-*Xylenol on Ethyl Phenylpropiolate.*

*Ethyl β-*m-*Xylenoxycinnamate,*



The action of ethyl phenylpropiolate (1 mol.) on a hot solution of sodium (1 at.) in an excess of *m*-xylenol takes place very readily. The sodium derivative of the phenol, which partly separates on adding the unsaturated ester, disappears. The dark red oil which is formed sets, on cooling, to a resin. After standing for some hours, it is agitated with dilute sulphuric acid and ether; the ethereal layer is then freed from the excess of the phenol by potash, the ether evaporated, and the remaining oil distilled in a vacuum. It boils at 225—226° under 10 mm. pressure, is colourless, and at 21°/21° has the density 1·0946. On analysis:

0·1877 gave 0·5300 CO_2 and 0·1180 H_2O. C = 77·0; H = 6·98.
$C_{19}H_{20}O_3$ requires C = 77·02; H = 6·76 per cent.

*β-*m-*Xylenoxycinnamic Acid,* $(\overset{[1:3]}{CH_3})_2C_6H_3\cdot\overset{[4]}{O}\cdot C(C_6H_5):CH\cdot CO_2H$.—The ester is hydrolysed when it is boiled with alcoholic potash for 2 hours. On adding dilute sulphuric acid to the alkaline fluid after evaporation of the alcohol on the water-bath, *β-m*-xylenoxycinnamic

acid is precipitated as a resin, which, on stirring with a little alcohol, sets to a solid. This dissolves in hot dilute alcohol, and the solution, on cooling, yields an emulsion from which colourless prisms gradually separate. The acid melts at 121—122° with evolution of gas. On analysis:

0·2000 gave 0·5575 CO_2 and 0·1080 H_2O. C = 76·02; H = 6·0.
$C_{17}H_{16}O_3$ requires C = 76·12; H = 5·97 per cent.

The *silver* salt is obtained as a white precipitate on mixing the solution of the acid in ammonia with silver nitrate; it is neither changed on exposure to light nor decomposed on drying at 100°. On analysis:

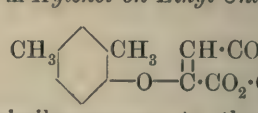
0·2994 left, on ignition, 0·0858 Ag. Ag = 28·66.
$C_{17}H_{15}O_3Ag$ requires Ag = 28·80 per cent.

β-m-*Xylenoxystyrene*, $(\overset{[1:3]}{CH_3})_2C_6H_3\cdot\overset{[4]}{O}\cdot C(C_6H_5):CH_2$.—*β*-*m*-Xylenoxycinnamic acid, on heating, loses carbon dioxide, and *β*-*m*-xylenoxystyrene is formed. It is a colourless oil with an aromatic odour, distils at 178° under 15 mm. pressure, and at 21°/21° has the density 1·0353. On analysis:

0·1700 gave 0·5343 CO_2 and 0·1090 H_2O. C = 85·71; H = 7·12.
$C_{16}H_{16}O$ requires C = 85·71; H = 7·14 per cent.

Action of the Sodium Derivative of m-*Xylenol on Ethyl Chlorofumarate.*

Ethyl m-*Xylenoxyfumarate*,



This compound is formed in a similar manner to the other aryl ethers of ethyl hydroxyfumarate, that is, by gradually adding ethyl chlorofumarate (1 mol.) to a hot solution of sodium (1 at.) in an excess of *m*-xylenol. The dark product, after treatment as in the former cases, yields a yellowish oil which boils at 202—203° under 17 mm. pressure, and at 21°/21° has the density 1·0978. On analysis:

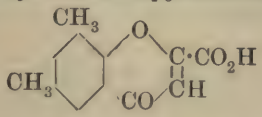
0·2033 gave 0·4892 CO_2 and 0·1263 H_2O. C = 65·62; H = 6·92.
$C_{16}H_{20}O_5$ requires C = 65·75; H = 6·85 per cent.

m-*Xylenoxyfumaric Acid*, $(\overset{[1:3]}{CH_3})_2C_6H_3\cdot\overset{[4]}{O}\cdot C(CO_2H):CH\cdot CO_2H$.—The ester is readily hydrolysed by boiling it with alcoholic potash. After the alkaline solution has been freed from alcohol by distillation on the water-bath, water is added to the residue, and then an excess of dilute sulphuric acid. The solid, which is precipitated, dissolves in boiling water with difficulty, but with great ease in alcohol or ether,

and crystallises from dilute alcohol in yellowish prisms which melt and decompose at 210°. On analysis:

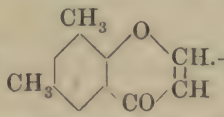
0·2025 gave 0·4539 CO_2 and 0·0955 H_2O. C = 61·13; H = 5·24.
$C_{12}H_{12}O_5$ requires C = 61·01; H = 5·08 per cent.

6 : 8-*Dimethyl*-1 : 4-*benzopyrone*-2-*carboxylic Acid*,



m-Xylenoxyfumaric acid dissolves in cold concentrated sulphuric acid, forming a red solution. After standing overnight, this is gradually poured into cold water, when a white, gelatinous precipitate is formed, which crystallises from dilute alcohol in colourless prisms. These melt and decompose at 278°, and are freely soluble in alcohol but insoluble in water. On analysis:

0·2028 gave 0·4916 CO_2 and 0·0860 H_2O. C = 61·11; H = 4·71.
$C_{12}H_{10}O_4$ requires C = 66·05; H = 4·59 per cent.

6 : 8-*Dimethyl*-1 : 4-*benzopyrone*,  —On heating the dimethylbenzopyronecarboxylic acid, it loses carbon dioxide, and a yellowish oil distils over which rapidly solidifies. The solid is freed from a small quantity of the acid which it contains by shaking the ethereal solution of the distillate with sodium carbonate. On evaporation of the ether, the dimethylpyrone remains behind; it crystallises from dilute alcohol in colourless needles which melt at 80—81° and dissolve in concentrated sulphuric acid, forming a colourless solution with a bluish fluorescence. On analysis:

0·1974 gave 0·5482 CO_2 and 0·1047 H_2O. C = 75·73; H = 5·89.
$C_{11}H_{10}O_2$ requires C = 75·80; H = 5·75 per cent.

Action of Sodium Phenolate on the Esters of β-Chlorocrotonic and β-Chloroisocrotonic Acids.

Ethyl β-Phenoxycrotonate, $CH_3{\cdot}C(O{\cdot}C_6H_5){:}CH{\cdot}CO_2{\cdot}C_2H_5$.—Sodium phenolate reacts with ethyl β-chlorocrotonate as readily as with ethyl chlorofumarate on adding the ester (1 mol.) to a hot solution of sodium (1 at.) in an excess of phenol. The dark oily product, when subjected to the same treatment as in the former cases, yields a colourless oil with a pleasant aromatic odour, which distils at 147—148°

under 14 mm. pressure, and at 21°/21° has the density 1·0726. On analysis :

0·1980 gave 0·5065 CO_2 and 0·1236 H_2O. C = 69·76 ; H = 6·93.
$C_{12}H_{14}O_3$ requires C = 69·90 ; H = 6·80 per cent.

The ester, on hydrolysis with alcoholic potash, is transformed into *β-phenoxycrotonic acid*, $CH_3{\cdot}C(O{\cdot}C_6H_5){:}CH{\cdot}CO_2H$. On adding dilute sulphuric acid to the alkaline solution, after evaporation of the alcohol, the acid is precipitated as a white solid which dissolves in ether or alcohol with great ease, but only sparingly in water, and crystallises from dilute alcohol in colourless needles melting at 155°. On analysis :

0·2105 gave 0·4971 CO_2 and 0·1062 H_2O. C = 67·28 ; H = 5·85.
$C_{10}H_{10}O_3$ requires C = 67·41 ; H = 5·62 per cent.

The *silver* salt is formed as a white precipitate, which is first gelatinous, but gradually becomes curdy, on adding silver nitrate to the solution of the acid in ammonia. The salt is insoluble in water, and has to be dried in a vacuum, since it turns brown when heated at 100°. On analysis :

0·2805 left, on ignition, 0·1065 Ag. Ag = 37·96.
$C_{10}H_9O_3Ag$ requires Ag = 37·89 per cent.

β-Phenoxycrotonic acid, as has been mentioned (p. 1186), when dissolved in concentrated sulphuric acid, or when boiled with dilute sulphuric acid, suffers a decomposition similar to that of the aryl ethers of β-hydroxycinnamic acid, and furnishes carbon dioxide, phenol, and acetone.

β-Phenoxypropylene, $CH_3{\cdot}C(O{\cdot}C_6H_5){:}CH_2$.—On heating β-phenoxycrotonic acid in a vacuum, it distils with partial decomposition ; this, however, is complete on distillation under the atmospheric pressure. The colourless oil so obtained, boils at 170°, and has an odour resembling that of phenyl mustard oil. On analysis :

0·2400 gave 0·7118 CO_2 and 0·1610 H_2O. C = 80·88 ; H = 7·45.
$C_9H_{10}O$ requires C = 80·60 ; H = 7·46 per cent.

As stated on p. 1186, ethyl β-chloro*iso*crotonate yields the same product as ethyl β-chlorocrotonate, when it is treated with sodium phenolate. The substance obtained from the former ester distils at 152° under 18 mm. pressure, as compared with 147—148° (under 14 mm. pressure) which we have found for the sample prepared from ethyl chlorocrotonate. Its composition, moreover, has been verified by the following analysis :

0·1938 gave 0·4960 CO_2 and 0·1178 H_2O. C = 69·80 ; H = 6·75.
$C_{12}H_{14}O_3$ requires C = 69·90 ; H = 6·80 per cent.

The identity of both specimens of ethyl β-phenoxycrotonate is also supported by the fact that the acids formed from them on hydrolysis have the same crystalline forms and melting points.

GONVILLE AND CAIUS COLLEGE,
CAMBRIDGE.

CXXVI.—*The Hydrobromides of Undecylenic Acid.*

By JAMES WALKER and JOHN S. LUMSDEN.

BRUNNER (*Ber.*, 1886, **19**, 2226), by the addition of hydrogen bromide to undecylenic acid, $C_{11}H_{20}O_2$, obtained a bromundecylic acid, $C_{11}H_{21}O_2Br$, which fused at 35°. No details of the mode of preparation or purification are given. The same acid is mentioned by Nördlinger (*Ber.*, 1890, **23**, 2357), but again no details are given. Nördlinger also, by the addition of hydrogen bromide to the methyl and ethyl esters of undecylenic acid, prepared the corresponding esters of a bromundecylic acid. As it has been proved with practical certainty that undecylenic acid has the formula $CH_2{:}CH{\cdot}[CH_2]_8{\cdot}CO_2H$, compounds obtained from it by the addition of hydrogen bromide must have one or other of the formulæ :

$$CH_2Br{\cdot}CH_2{\cdot}[CH_2]_8{\cdot}CO_2H \text{ and } CH_3{\cdot}CHBr{\cdot}[CH_2]_8{\cdot}CO_2H.$$

Nördlinger, on the strength of the rule that the halogen atom in such additions generally takes up the position more remote from the carboxyl group, assumes that Brunner's acid has the formula $CH_2Br{\cdot}[CH_2]_9{\cdot}CO_2H$ and that the esters which he himself prepared are the esters of this acid. Since these esters have been made the starting point for determining the constitution of various substances, it is plainly of importance to know if Nördlinger's assumptions are justified. In the present paper, it is shown that the acid

$$CH_2Br{\cdot}[CH_2]_9{\cdot}CO_2H$$

is not Brunner's acid, which has in all probability the other constitution, $CH_3{\cdot}CHBr{\cdot}[CH_2]_8{\cdot}CO_2H$. Both these acids are simultaneously formed by the addition of hydrogen bromide to undecylenic acid, and no doubt the esters of both are produced by the addition of hydrogen bromide to undecylenic esters, a circumstance which would explain the divergent results obtained by different observers in syntheses involving their use.

Addition of Hydrogen Bromide to Undecylenic Acid.

The hydrogen bromide which we used in the following experiments was in all cases free from bromine, and dried by means of phosphoric oxide.

Addition without the use of a Solvent.—The following is a typical experiment. Seven grams of undecylenic acid were saturated with hydrogen bromide at the ordinary temperature. The acid fused and became slightly warm. Absorption ceased when 3·5 grams of the gas had been taken up. Dry air was then led through the liquid product to remove the excess of hydrogen bromide. This occasioned a loss of 0·5 gram, so that 7 grams of undecylenic acid had united with 3·0 grams of hydrogen bromide, the calculated quantity being 3·1 grams. After remaining for some time in a vacuous desiccator, the liquid partially solidified, and the crystals (4 grams) were separated from the oil (6 grams) by filtration.

The crude crystals were spread on porous tiles to remove the oil which still adhered to them, and were recrystallised from warm light petroleum. The substance separated in clusters of needles which melted at 50°.

The oil did not solidify at the laboratory temperature even after long-continued standing, but crystallised on cooling to 0°. The crystals were washed on the ice-cooled filter with cooled light petroleum, and were then spread on porous tiles. On recrystallisation from light petroleum, they melted at 35°.

In this experiment, Brunner's acid was formed in about equal proportion with another acid of higher melting point. The proportions of the two acids vary very much in different experiments, sometimes one, sometimes the other, preponderating.

Addition in Ethereal Solution.—Seven grams of undecylenic acid were dissolved in anhydrous ether, and the solution saturated at the ordinary temperature with hydrogen bromide, the excess of which was afterwards removed by a current of dry air. On evaporation of the ether, the residue solidified, and was purified by spreading on a porous tile and recrystallisation from light petroleum. Five grams of Brunner's acid melting at 35° were thus obtained. The presence of the ether seems to favour the formation of the isomeride of lower melting point.

Addition in Toluene Solution.—Twenty-five grams of undecylenic acid were dissolved in 20 grams of toluene, the solution cooled in ice, and saturated with hydrogen bromide. When saturation was complete, a solid separated, which was filtered off, thoroughly mixed with a little light petroleum at 0°, and refiltered. After drying on a tile, its weight was found to be 16 grams and its melting point 49—50°.

The filtrates on cooling to 0° deposited a further amount of solid, which was purified as already mentioned. In all, 26·5 grams of the acid of higher melting point were obtained from the 25 grams of undecylenic acid, and this we have found to be the best method of preparing it.

ω-Bromundecylic Acid, $CH_2Br\cdot[CH_2]_9\cdot CO_2H$.

This acid, prepared in toluene solution in the manner just detailed, is insoluble in water, but freely soluble in the ordinary organic solvents, for example, alcohol, ether, chloroform, or benzene. Whilst easily soluble in warm light petroleum, it is only sparingly so at the ordinary temperature, and very sparingly so at 0°. Light petroleum therefore forms the most convenient solvent for its recrystallisation. It usually separates in clusters of fine needles, which, when pure, melt sharply at 51° without discoloration or evolution of gas. The substance gave the following numbers on analysis:

0·1472, heated in a Carius tube with 0·4323 $AgNO_3$, required 19·9 c.c. of decinormal NH_4CNS to precipitate the excess of $AgNO_3$. Br = 30·05.

$C_{11}H_{21}O_2Br$ requires Br = 30·19 per cent.

The substance may be warmed either by itself or in organic solvents to a temperature considerably above its melting point without noteworthy evolution of hydrogen bromide occurring. The aqueous solutions of its alkali salts also are comparatively stable, showing little tendency to the separation of bromide and regeneration of undecylenic acid.

ω-Hydroxyundecylic Acid, $CH_2(OH)\cdot[CH_2]_9\cdot CO_2H$.

Thirteen grams of ω-bromundecylic acid were dissolved in the calculated quantity of normal sodium hydroxide solution, and the resulting liquid was warmed for 12 hours at 60—70° with excess of freshly precipitated silver hydroxide, the mixture being constantly agitated by means of a Witt stirrer. The action was then complete, bromine in any form being absent from the solution. The silver compounds were removed by filtration, treated with a little warm dilute sodium hydroxide solution, and again filtered. The filtrates were united, and acidified with nitric acid, whereupon a solid acid separated, which was filtered off, washed with water, dried on porous tiles, and crystallised from benzene. On recrystallisation from much hot water, the acid separated in clusters of very long, fine needles, and melted at 70°. From the above quantity of bromundecylic acid, 5·5 grams of the purified hydroxy-acid were obtained.

0·0801 gave 0·0800 H_2O and 0·1922 CO_2. C = 65·43; H = 11·10.

$C_{11}H_{22}O_3$ requires C = 65·35; H = 10·89 per cent.

0·1206 of the calcium salt gave 0·0372 $CaSO_4$. Ca = 9·07.

$(C_{11}H_2O_3)_2Ca$ requires Ca = 9·05 per cent.

The acid is thus monobasic, and has the composition of a hydroxyundecylic acid.

It is easily soluble in alcohol or ether, moderately so in benzene, separating readily from a warm solution, and sparingly in light petroleum. One hundred parts of water at 20° dissolve 0·04 part of the acid. As it is more than 20 times as soluble in boiling water, it can easily be purified by crystallisation from this solvent.

A solution of the sodium salt containing 1 part in 200 is freely precipitated on addition of soluble salts of barium, calcium, strontium, silver, zinc, or mercury. The barium, strontium, calcium, and silver salts are much more soluble at the boiling point than at the ordinary temperature. The calcium salt was purified for analysis by recrystallisation from boiling water. The solution of sodium salt of the above strength affords only a slight precipitate with a soluble magnesium salt. A more concentrated solution of the sodium salt, however, gave a curdy, somewhat stringy, precipitate, which dissolved slightly on heating, and was reprecipitated in a granular form on cooling the filtered solution.

As this hydroxyundecylic acid is derived from the straight-chain undecylenic acid, it also has its carbon atoms in a straight-chain. On oxidation with chromium trioxide, it is converted into a dicarboxylic acid having the same number of carbon atoms as itself. The hydroxyl which it contains is therefore part of a primary alcohol group. The acid therefore must have the constitution $CH_2(OH)\cdot[CH_2]_9\cdot CO_2H$, and consequently the bromo-acid from which it was derived must be $CH_2Br\cdot[CH_2]_9\cdot CO_2H$.

n-*Nonanedicarboxylic Acid*, $CO_2H\cdot[CH_2]_9\cdot CO_2H$.

One gram of ω-hydroxyundecylic acid was dissolved in glacial acetic acid, and to the solution were added 10 c.c. of a 1 : 10 solution of chromium trioxide in glacial acetic acid. A slight rise of temperature was observed when the solutions were mixed. The mixture was allowed to remain overnight, and on the following morning was gently warmed to complete the oxidation. The solution was then poured into cold water, when a white precipitate separated. This was filtered off, washed with water, dried on porous tiles, and recrystallised first from benzene and then from boiling water. In this way, 0·6 gram of an acid melting at 110° was obtained. Analysis yielded the following results.

0·1323 gave 0·2968 CO_2 and 0·1112 H_2O. C = 61·17; H = 9·34.
$C_{11}H_{20}O_4$ requires C = 61·11; H = 9·26.

0·1545 required 28·5 c.c. of *N*/20 NaOH for neutralisation. Replaceable H = 0·922; calculated for $C_9H_{18}(CO_2H)_2$ replaceable H = 0·926.

The substance is thus a nonanedicarboxylic acid, and its derivation from undecylenic acid shows it to have the normal structure.

n-Nonanedicarboxylic acid resembles sebacic acid, and the other higher members of the series of normal saturated dibasic acids in appearance and properties. It is soluble in alcohol or ether, can be crystallised readily from warm benzene, and is very sparingly soluble in light petroleum. One hundred parts of water at 20° dissolve 0·014 part of the acid. It is much more soluble in boiling water, from which it separates on cooling in lustrous scales, indistinguishable in appearance from those obtained under similar conditions from *n*-decanedicarboxylic acid and *n*-brassylic acid.

The melting point of the purified substance is 110°, and falls into place in the series of melting points of the group of normal acids to which it belongs, thus :

Acid (even).		Melting point.	Melting point.	Acid (odd).	
Succinic	$C_4H_6O_4$	181°	98°	$C_5H_8O_4$	Glutaric.
Adipic	$C_6H_{10}O_4$	149	103	$C_7H_{12}O_4$	Pimelic.
Suberic	$C_8H_{14}O_4$	141	107	$C_9H_{16}O_4$	Azelaic.
Sebacic	$C_{10}H_{18}O_4$	133	110	$C_{11}H_{20}O_4$	Nonanedicarboxylic.
Decanedicarboxylic.....	$C_{12}H_{22}O_4$	127	113	$C_{13}H_{24}O_4$	Brassylic.
Dodecanedicarboxylic ..	$C_{14}H_{26}O_4$	123			

A solution of the sodium salt containing 0·6 gram in 100 c.c. was precipitated in the cold by solutions of calcium, zinc, silver, or mercuric salts. Barium salts gave no immediate precipitate in the cold, but a granular precipitate formed on heating the solution to the boiling point. Magnesium salts gave no precipitate in either hot or cold solution. A solution containing 3 grams of the sodium salt in 100 c.c. gave a slight precipitate with magnesium nitrate in the cold, which greatly increased in bulk on heating the solution to 100°. The calcium salt is very nearly equally soluble in hot and in cold water.

Bromundecylic Acid, m. p. 35°.

This acid, originally prepared by Brunner, is by no means so stable as the ω-bromundecylic acid melting at 51°. It melts sharply at 35°, but the fusion is usually accompanied by the formation of minute bubbles of gas, no doubt hydrogen bromide. Traces of hydrogen bromide are lost on warming the liquid, either by itself or in solution. Analysis of a specimen recrystallised from warm light petroleum gave 29·9 per cent. of bromine instead of 30·2 per cent. required by the formula $C_{11}H_{21}O_2Br$.

The acid is freely soluble in the ordinary organic solvents, but insoluble in water. It is considerably more soluble in light petroleum than the isomeric ω-bromundecylic acid, and can easily be crystallised from this solvent, the crystals assuming the form of thin plates or

oblique prisms. In contact with an alkaline solution, it readily loses the elements of hydrogen bromide with simultaneous formation of undecylenic acid. Thus an attempt was made to convert it into the corresponding hydroxy-acid by treatment of its sodium salt with silver hydroxide. The action was conducted at the ordinary temperature, and took a fortnight for completion, the product being then worked up as detailed under ω-hydroxyundecylic acid. The resulting acid was liquid, and only partially solidified on long standing. It was found to be unsaturated, and analysis showed it to consist of impure undecylenic acid.

This tendency of the bromo-acid to revert to undecylenic acid made direct proof of its constitution difficult to procure. The tendency to lose hydrogen bromide would of itself, however, indicate that the bromine is not primary. Moreover, we know the primary bromo-acid, and since the mode of formation from undecylenic acid admits of only two possible constitutions, and the possibility of stereoisomerism is excluded, it is practically certain that the bromundecylic acid melting at 35° has the constitution $CH_3 \cdot CHBr \cdot [CH_2]_8 \cdot CO_2H$, in opposition to Nördlinger's assumption.

Synthesis of n-*Brassylic Acid.*

Both Komppa (*Ber.*, 1901, **34**, 897) and Krafft and Seldis (*Ber.*, 1900, **33**, 3571), starting from the ester obtained by the addition of hydrogen bromide to ethyl undecylenate, have by means of a malonic ester synthesis prepared undecanedicarboxylic acids, which both originally held to be the normal acid, for both postulated that the bromundecylic ester with which they worked was the ω-derivative. The acids which they obtained, however, differed entirely from each other; that of Krafft and Seldis melted at 113—114°, being identical with ordinary brassylic acid, whilst Komppa's acid melted at 82° and gave entirely different derivatives.

In order to ascertain definitely which was the normal acid, we performed the synthesis with an ester prepared from pure ω-bromundecylic acid. In converting this acid into its ethyl ester, it is necessary to employ more alcohol than usual, for although it dissolves readily enough in pure alcohol, it is thrown out of solution when sulphuric or hydrochloric acid is added. Five grams of the acid were heated with 150 c.c. of alcohol and 5 c.c. of sulphuric acid on the water-bath for 6 hours. This yielded 4·5 grams of the ethyl ester, boiling at 188—190° under 18 mm. pressure.

On performing a malonic ester synthesis with this amount in the usual way, the liquid became neutral after 20 hours' heating. The mixed esters were extracted and dried, and saponified by adding

them while hot to a boiling solution of alcoholic potash. A white precipitate of potassium salt separated in a few minutes. From this the tribasic acid was liberated by hydrochloric acid, and appeared as a pure white, bulky, flocculent precipitate which melted when the water was warmed, and solidified on cooling. The dry substance melted in bulk at about 60°, and in a melting point tube at 70°, with evolution of carbon dioxide, which became very brisk above 100°. After all the carbon dioxide had been driven off, the residual dibasic acid was recrystallised from boiling water. It formed pearly scales melting at 111—112°. On recrystallisation from warm benzene, it melted at 112—113°, and agreed in its other properties with the brassylic acid derived from erucic acid, which has therefore undoubtedly the normal structure.

No doubt the esters employed by Krafft and Seldis on the one hand, and Komppa on the other, although apparently prepared in the same way, contained different proportions of the two possible bromundecylic esters (compare p. 1191), so that in the one case the normal undecanedicarboxylic acid resulted from a malonic ester synthesis, and in the other case an isomeric acid.

Fileti and Ponzio (abstract in *Ber.*, 1893, **26**, Ref. 811, from *J. pr. Chem.*, [ii], **48**, 323) give the solubility of brassylic acid in 100 parts of water at 24° as 0·74. This is obviously erroneous, as even acids so low in the series as suberic and sebacic acids do not attain even approximately this degree of solubility. An experiment with our synthetic brassylic acid gave a solubility of 0·004 in 100, which is in harmony with the results obtained for the other members of the series (see following paper).

University College,
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CXXVII.—n-*Decanedicarboxylic Acid.*

By James Walker and John S. Lumsden.

The following research was begun by us more than two years ago, and was then completed as far as the electrosynthesis of *n*-decanedicarboxylic acid from pimelic acid. The properties of the electrosynthetic acid differed, however, in so many particulars from those of the acid prepared by Nördlinger from his bromundecylic esters (*Ber.*, 1890, **23**, 2357; compare preceding paper), that, notwithstanding their general resemblance, we were uncertain of the identity of the two acids, and were compelled to undertake a revision of Nördlinger's work. In the

meantime, an abstract of a paper by Komppa appeared (*Chem. Centr.*, 1899, ii, 1016; from *Festschrift. Polyt. Instit. Helsingfors*, April, 1899), in which it was stated that he had prepared the electrosynthetic acid, and found its properties to be identical with those of the acid described by Nördlinger. We were at a loss to account for this divergence from our own results, and awaited the details of Komppa's research. These have now been published (*Ber.*, 1901, **34**, 895), and as we have, meantime, prepared *n*-decanedicarboxylic acid from ω-bromundecylic acid, we are at present in a position to make a direct comparison of this with our electrosynthetic acid, and also to compare both of these with the acids of Nördlinger and Komppa.

As Komppa performed the electrolysis of ethyl potassium pimelate with a comparatively small quantity (6·5 grams) of material, and investigated none of the intermediate and subsidiary products, we here give a brief account of the preparation and electrolysis of ethyl potassium pimelate, as carried out by ourselves.

Preparation of n-*Pimelic Acid from Salicylic Acid.*

When salicylic acid is reduced by sodium in amyl alcohol, a considerable proportion of it is converted into *n*-pimelic acid according to the empirical equation,

$$C_7H_6O_3 + H_2O + 4H = C_7H_{12}O_4$$

(Einhorn and Lumsden, *Annalen*, 1895, **286**, 257). This reaction forms a convenient method of preparing *n*-pimelic acid when carried out according to the following directions.

Salicylic acid is boiled for 2 hours with five times its weight of dried fusel oil and half its weight of sulphuric acid. By this means, it is mostly converted into esters, which are more readily reducible than the acid itself. After cooling, the sulphuric acid is washed out from the oil with water, and finally with dilute sodium carbonate solution (which also removes a little untransformed salicylic acid), and the residual liquid is then dried over anhydrous sodium sulphate. The solution is diluted with fusel oil until it occupies 100 c.c. for each 7 grams of salicylic acid originally taken.

The reduction is then effected as follows. A litre flask of Jena glass is fitted with a V-shaped adapter of half-inch bore, the sloping limb of which is attached to a reflux condenser. A dropping-funnel is fitted by means of a cork into the upright limb, and can be removed as required for the introduction of pieces of sodium. Ten grams of sodium in large pieces and 50 c.c. of fusel oil are heated in the flask on an asbestos air-bath to the boiling point of the alcohol, and the solution of salicylic esters is then dropped in slowly from the tap funnel until 150 c.c. have been added. When the first charge of sodium is reduced

to a small bulk, a second charge of 10 grams is added, and the heating continued until all the sodium disappears. The operation lasts about 3 hours, and during this time the flask must be occasionally shaken, to prevent the sodium compounds which separate out from hardening on the walls of the flask.

When the sodium has disappeared, the contents of the flask are cooled to a little below 100°, and an equal bulk of water is added to decompose the sodium amyloxide and dissolve out the sodium salts produced by the reduction. The aqueous layer is separated from the oil, which is subsequently washed out twice with its own bulk of water, the aqueous extracts being added to the original aqueous solution. The aqueous liquid is then boiled to reduce its bulk and to remove the fusel oil which it retains in solution. After cooling, the liquid is strongly acidified with hydrochloric acid. An oily acid separates at once, and some salicylic acid crystallises out on standing. These are removed by filtration and rejected. The filtrate is then boiled down until sodium chloride begins to separate, when it is cooled and thrice extracted with ether. The ether is distilled off from the extract, and the residue dissolved in a little boiling water, any oil which remains undissolved being filtered off. On cooling, a little salicylic acid usually separates. This is removed by filtration, and the filtrate concentrated by evaporation until pimelic acid begins to crystallise out. The average yield of pimelic acid is 4·5—5 grams from 10·5 grams of salicylic acid.

It is inadvisable to work with pure amyl alcohol, or with larger quantities than those given. As three or four reductions, however, can be carried on simultaneously, and the products worked up together, the preparation of a quantity of pimelic acid is not so tedious as might appear from the above description.

Preparation and Electrolysis of Ethyl Potassium Pimelate.

Pimelic acid (100 grams) was converted into the diethyl ester (103 grams obtained) by means of ethyl alcohol and hydrochloric acid. The diethyl ester thus prepared was dissolved in twenty-five times its weight of ethyl alcohol, and half saponified at the ordinary temperature by treatment with the calculated quantity of potassium hydroxide in four successive portions (compare Walker, Trans., 1892, **51**, 710). Ten grams of the ester were recovered unchanged, so that 10 grams had been converted into the dipotassium salt, and 80 grams into the ethyl potassium salt.

Ethyl Hydrogen Pimelate, $CO_2H{\cdot}[CH_2]_5{\cdot}CO_2Et$.—A small quantity of the aqueous solution of the mixed potassium salts was acidified with hydrochloric acid, and the liberated acids extracted with ether. The acids were then converted into the corresponding calcium salts by

warming with water and precipitated calcium carbonate until the aqueous solution became neutral. Ethyl calcium pimelate is freely soluble in water (less so at the boiling point than at the ordinary temperature), whereas calcium pimelate is sparingly soluble. The calcium salts were thus to a large extent separated from each other. Ethyl hydrogen pimelate, separated from the solution of ethyl calcium pimelate by acidification, is a colourless oil which does not solidify at 0°. In this respect it resembles ethyl hydrogen adipate, and differs from ethyl hydrogen suberate and ethyl hydrogen sebate, which are solids melting at 18° and 38° respectively (Walker, *loc. cit.*, p. 713). It is easily miscible with the ordinary organic solvents, but only sparingly soluble in water.

0·1 gram required 10·9 c.c. *N*/20 HCl for neutralisation; replaceable H = 0·54 per cent.; calculated for $CO_2Et\cdot[CH_2]_5\cdot CO_2H$ replaceable H = 0·53 per cent. The substance was therefore nearly free from pimelic acid.

A solution which contained 75 grams of ethyl potassium pimelate, together with dipotassium pimelate as impurity, was dissolved in 100 c.c. of water, and electrolysed with a stout platinum wire as anode, the current averaging 10 amperes and the temperature being kept below 30°. In this way, 26 grams of an oil were obtained which consisted mainly of the ethyl esters of two acids formed at the anode in the normal manner as follows:

$$2CO_2Et\cdot[CH_2]_5\cdot CO_2 = \underset{\text{Ethyl } n\text{-decanedicarboxylate.}}{CO_2Et\cdot[CH_2]_{10}\cdot CO_2Et} + 2CO_2.$$

$$2CO_2Et\cdot[CH_2]_5\cdot CO_2 = \underset{\text{Ethyl } n\text{-pentenecarboxylate.}}{CO_2Et\cdot[CH_2]_3\cdot CH{:}CH_2} + CO_2Et\cdot[CH_2]_5\cdot CO_2H + CO_2.$$

The esters were dissolved out in ether, washed, dried with calcium chloride, and after evaporation of the ether distilled under reduced pressure. As usual, the esters separated roughly on fractionation into a low boiling and a high boiling portion, which were saponified separately with alcoholic potash. On acidification, the portion of lower boiling point yielded an oily acid containing a little solid, and that of higher boiling point a solid acid contaminated with a little oil.

n-*Pentenecarboxylic Acid*, $CH_2{:}CH\cdot[CH_2]_3\cdot CO_2H$.—The liquid acid, which was only obtained in small quantity, was found to be easily volatile with steam, and was therefore separated from the solid acid by steam distillation. The oil thus obtained boiled between 215° and 220°, and did not solidify in a good freezing mixture. It mixed readily with the ordinary organic solvents, but was comparatively slightly soluble in water. It absorbed bromine in chloroform solution, and its sodium salt at once decolorised potassium permanganate in aqueous solution at the ordinary temperature.

0·1264 gave 0·2942 CO_2 and 0·1016 H_2O. C = 63·5; H = 8·9.
$C_6H_{10}O_2$ requires C = 63·2; H = 8·8 per cent.

The small quantity at our disposal precluded further purification, but the above data are sufficient to show that the acid is *n*-pentenecarboxylic acid, a normal product of the electrolysis.

n-*Decanedicarboxylic Acid*, $CO_2H\cdot[CH_2]_{10}\cdot CO_2H$.—The solid acid obtained from the fraction of higher boiling point, which constituted by far the larger proportion of the mixed esters, was freed from the liquid acid by steam distillation. It was finally dissolved in much boiling water, from which it separated on cooling in the form of pearly scales melting at 126·5—127°. Komppa gives 125·5—127° as the melting point of his electrosynthetic acid.

0·1551 gave 0·3555 CO_2 and 0·1320 H_2O. C = 62·52; H = 9·46.
$C_{12}H_{22}O_4$ requires C = 62·61; H = 9·56 per cent.
0·1428 barium salt gave 0·0902 $BaSO_4$. Ba = 37·2.
$C_{12}H_{20}O_4Ba$ requires Ba = 37·5 per cent.

The acid is thus the normal product of the electrosynthesis.

Preparation of n-*Decanedicarboxylic Acid from* ω-*Bromundecylic Acid.*

Nördlinger states that Brunner's bromundecylic acid cannot be converted by the action of potassium cyanide into the corresponding cyanundecylic acid. He consequently employed for this transformation the methyl and ethyl esters obtained by the addition of hydrogen bromide to the corresponding esters of undecylenic acid (see preceding paper). In view, however, of the comparative stability of the ω-bromo-acid, we considered it probable that replacement of bromine by cyanogen could be effected in a neutral salt of the acid; this we found to be the case.

5·3 grams of ω-bromundecylic acid were dissolved in 20 c.c. of normal caustic soda solution, 1·6 grams of potassium cyanide were added, and the liquid was then made up to 100 c.c. The solution was heated on the water-bath for 12 hours, during which time a considerable amount of a brownish, flocculent precipitate was deposited. This was removed by filtration, and the filtrate saturated with hydrogen chloride. An oily cyano-acid separated, which partially solidified on cooling. After heating the mixture on the water-bath in a reflux apparatus for 3 hours, the oil was completely transformed into a cake of small crystals. The mixture on cooling deposited more crystals, which were filtered off together with the original cake, washed, and recrystallised from boiling water. The substance obtained melted at 123—124°, but on subsequent recrystallisation, the melting point rose to 126·5°.

Nördlinger gives 124·5—125·5° for his acid. 1·65 grams of the pure substance were thus obtained.

0·0900 gave 0·2060 CO_2 and 0·0776 H_2O. C = 62·42; H = 9·58.
$C_{12}H_{22}O_4$ requires C = 62·61; H = 9·56 per cent.

0·1458 required 25·1 c.c. $N/20$ NaOH for neutralisation. Replaceable H = 0·861. Calculated for $C_{10}H_{20}(CO_2H)_2$ replaceable H = 0·869.

On direct comparison, the acid was found to be identical in every respect with the electrosynthetic acid. This fact is conclusive evidence of the normal structure of undecylenic acid, and affords additional confirmation of the formulæ ascribed to the various substances mentioned in the preceding paper.

Nördlinger obtained a very impure product from the esters which he employed, and consequently a very small yield of the purified decanedicarboxylic acid. On the other hand, the yield from the sodium salt of ω-bromundecylic acid is equal to 40 per cent. of the theoretical, and the substance is at once obtained in a state approximating to purity.

Solubility of n-*Decanedicarboxylic Acid.*—The chief point in which Nördlinger and Komppa have obtained results in absolute discordance from ours is the solubility of the acids in water. This point is of importance, as it affords the only available numerical means (besides the melting point) for a comparison of their acid with ours. The solubility of our electrosynthetic acid is exactly that of the acid we prepared from ω-bromundecylic acid, and yet it is entirely divergent from the solubility of the acids obtained in similar ways by Nördlinger and Komppa, as the following numbers show:

	Nördlinger.	Komppa.	W. and L.
100 parts of water dissolve at 23°.....	0·005	0·0059	0·003
„ „ „ 100°.....	0·113	0·105	0·368

It thus appears that our acid is less soluble at 23°, and more soluble at 100°, than Nördlinger's and Komppa's acids. The difference in solubility at the lower temperature need not, however, be insisted on, as the magnitude measured is very small. On the other hand, the difference at 100° is far too great to be explained by any ordinary experimental error. Thus Komppa states that 100 c.c. of the solution saturated at 100° required 9·2 c.c. of decinormal soda solution for neutralisation, whilst a similar quantity of the saturated solution of our acid would require more than 30 c.c.

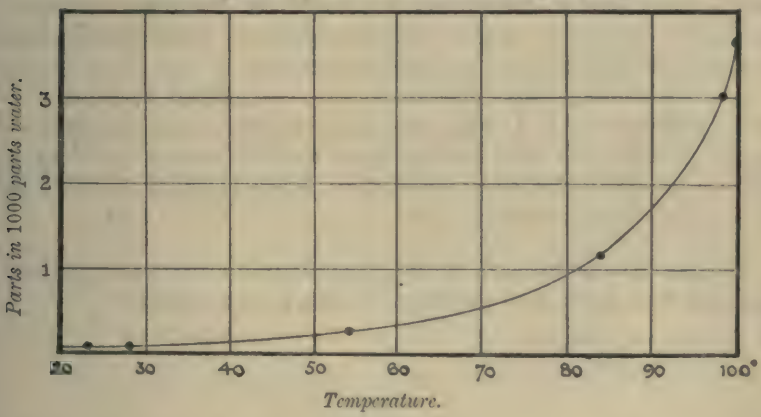
As we found the solubility of the acid near the boiling point varied very rapidly with the temperature, we determined the solubility at different intermediate temperatures, with the following results:

Temperature.	Parts dissolved by 100 parts of water.
23°	0·003
28	0·005
54	0·027
84	0·120
98	0·306
100	0·368

In each case, the solubility was determined by titrating a weighed quantity of the saturated solution by means of a twentieth-normal solution of caustic soda which had been standardised against the acid itself, phenolphthalein being used as indicator. At 54° and above, the filtration was conducted by means of a small suction filter immersed in the liquid itself.

The accompanying curve shows that our acid has a solubility at 82° equal to that given by Komppa and Nördlinger for 100°.

Solubility curve of normal decanedicarboxylic acid.



It is well known that the solubility of the members of the series of normal saturated dibasic acids with an even number of carbon atoms is smaller than the solubility of the members with an odd number of carbon atoms. This regularity persists with the higher members of the series, as we see from the following table, which incorporates the solubility results for the ordinary temperature given in this and the preceding paper.

Acid (even).		Solubility (parts in 100 of water).			Acid (odd).
Adipic	$C_6H_{10}O_4$	1·5	4·5	$C_7H_{12}O_4$	Pimelic
Suberic	$C_8H_{14}O_4$	0·14	0·12	$C_9H_{16}O_4$	Azelaic
Sebacic	$C_{10}H_{18}O_4$	0·01	0·014	$C_{11}H_{20}O_4$	Nonanedicarboxylic
Decanedicarboxylic...	$C_{12}H_{22}O_4$	0·003	0·004	$C_{13}H_{24}O_4$	Brassylic

Salts of n-*Decanedicarboxylic Acid.*—The description given by Nördlinger of the salts of his acid differs in many points of detail from what we found with the acid we had prepared, although there is a general resemblance in behaviour. For our experiments, we used a solution containing 0·64 gram of sodium salt in 100 c.c. With calcium nitrate, this gave a flocculent precipitate which settled readily; no further precipitate appeared when the clear liquid was boiled. Nördlinger states that both the calcium and barium salts are less soluble in boiling than in cold water. This is certainly the case to a slight extent with the barium salt, but we were unable to detect, in the case of the calcium salt, any appreciable difference in solubility at the ordinary temperature and at the boiling point. Strontium nitrate gave no precipitate at the ordinary temperature with the above solution, but gave a very slight precipitate on boiling. Magnesium nitrate gave no precipitate at any temperature; but a solution containing four times as much sodium salt gave a precipitate with this reagent on standing. Mercuric chloride gave a bulky, finely divided, precipitate, which did not coagulate readily on heating. Nördlinger states that his acid gave no precipitate with mercuric chloride, but only a slight opalescence.

Notwithstanding these differences, we are inclined to think that both Nördlinger and Komppa had *n*-decanedicarboxylic acid in their hands, Nördlinger's acid having been derived from a quantity of ω-bromundecylic ester, which must have been contained in the ester he prepared from undecylenic ester.

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CXXVIII.—*The Action of Sodium Methoxide and its Homologues on Benzophenone Chloride and Benzal Chloride.*

By JOHN EDWIN MACKENZIE, D.Sc., Ph.D.

IN a previous communication to the Society (Trans., 1896, **69**, 985), a description was given of the preparation of dimethoxydiphenylmethane by the action of sodium methoxide on benzophenone chloride according to the equation $(C_6H_5)_2CCl_2 + 2CH_3{\cdot}ONa = (C_6H_5)_2C(O{\cdot}CH_3)_2 + 2NaCl$, and of di-ethoxy- and dibenzoxy-diphenylmethane, using sodium ethoxide

and benzoxide respectively instead of methoxide. In continuing this investigation, dipropyloxy-, di*iso*butyloxy-, and dihydroxy-tetraphenylmethane have been prepared, and for the sake of comparison a number of experiments with benzal chloride have been carried out. The action of sodium methoxide and its homologues on benzal chloride was first investigated by Wicke (*Annalen*, 1857, **102**, 356), who prepared dimethoxy-, diethoxy-, and diamyloxy-benzylidenes, the reaction proceeding thus: $C_6H_5\cdot CHCl_2 + 2CH_3\cdot ONa = C_6H_5\cdot CH(O\cdot CH_3)_2 + 2NaCl$. Some years later, Limpricht, in a research on the chlorine substitution products of toluene (*Annalen*, 1886, **139**, 319), repeated Wicke's work, but was unable to obtain products free from chlorine. This being so, and no record of the yield of the products obtained by Wicke being given, it was thought advisable to try these experiments again under various conditions. Following Wicke's instructions, it was found that the reaction took place under the ordinary pressure as represented, but that the benzal chloride only disappeared on repeated treatment with sodium methoxide.*

On the other hand, when benzal chloride was heated with sodium ethoxide under pressure, a different reaction took place, ethyl chloride, benzaldehyde, and sodium chloride being the products. The change may be represented thus:

$$C_6H_5\cdot CHCl_2 + C_2H_5\cdot ONa = C_2H_5Cl + C_6H_5\cdot CHO + NaCl.$$

By using the sodium compounds of different alcohols, the corresponding chlorides were produced.

That this reaction does not apply to phenols would appear from the work of Fosse (*Compt. rend.*, 1900, **130**, 725 and 1194), who obtained diphenoxyethylidene by heating ethylidene chloride and sodium phenate in sealed tubes at 120°, according to the equation,†

$$CH_3\cdot CHCl_2 + 2C_6H_5\cdot ONa = CH_3\cdot CH(O\cdot C_6H_5)_2 + 2NaCl.$$

As in benzophenone chloride and benzal chloride both halogen atoms are attached to the same carbon atom, it was thought that it would be interesting to see what happened when the halogen atoms

* In the case of sodium benzoxide, the only product separated was stilbene, and that only in minute quantity. The reaction would thus appear to be expressed in part by the equation:

$$2C_6H_5\cdot CHCl_2 + 4C_6H_5\cdot CH_2\cdot ONa = 4NaCl + C_6H_5\cdot CH{:}CH\cdot C_6H_5 + 2C_6H_5\cdot CH_2\cdot OH + C_6H_5\cdot CHO.$$

† That this should be so is rather curious in view of the fact that when benzal chloride and phenol are heated together, they form dihydroxytriphenylmethane according to the equation:

$$C_6H_5\cdot CHCl_2 + 2C_6H_5\cdot OH = C_6H_5\cdot CH(C_6H_4\cdot OH)_2 + 2HCl,$$

and that benzophenone chloride gives a similar compound with either phenol or sodium phenoxide.

are attached to different carbon atoms. In the case of ethylene dibromide, the reaction would be expected to take place thus:

$$CH_2Br{\cdot}CH_2Br + 2C_2H_5{\cdot}ONa = CH_2(O{\cdot}C_2H_5){\cdot}CH_2(O{\cdot}C_2H_5) + 2NaBr,$$

but no record of experiment showing this to be so is known to the author. Diethoxyethylidene has, however, been prepared by Henry (*Compt. rend.*, 1885, 100, 1007) from an intermediate product in this way:

$$CH_2I{\cdot}CH_2(O{\cdot}C_2H_5) + C_2H_5{\cdot}ONa = CH_2(O{\cdot}C_2H_5){\cdot}CH_2(O{\cdot}C_2H_5) + NaI.$$

On heating ethylene dibromide with sodium ethoxide under pressure, however, it was found that acetylene was produced, reaction taking place thus:

$$CH_2Br{\cdot}CH_2Br + 2C_2H_5{\cdot}ONa = CH{:}CH + 2C_2H_5{\cdot}OH + 2NaBr.$$

The production of acetylene in a similar fashion, using sodium *iso*amyloxide instead of ethoxide, is recorded by Sawitch (*Jahresber.*, 1861, 646).

I. *Action of Sodium Alkyloxides on Benzophenone Chloride.*

Dipropyloxydiphenylmethane, $(C_6H_5)_2C(O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3)_2$.

In preparing this substance, 3·7 grams of sodium were dissolved in 40 grams of propyl alcohol, and to the cold product 19 grams of benzophenone chloride were added. The mixture was gradually heated to a temperature of 95°, when a violent action took place, and then kept at 120° for 7 hours, at the end of which time the supernatant liquid still gave an alkaline reaction. The liquid was filtered from the salt which had separated, the latter being washed three times with small quantities of propyl alcohol. The filtrate was then distilled under reduced pressure to remove the excess of propyl alcohol. The residue, which was a viscous, brown oil, was diluted by the addition of a little ethyl alcohol, filtered from some salt, and distilled, 7·9 grams of a colourless oil boiling at 200—210° under 40 mm. pressure being collected. The yellowish, semi-solid, strongly alkaline substance remaining in the distilling flask was distilled with steam. From the milky distillate, crystals separated which melted at 32—34°, and boiled at 204° under 40 mm. pressure. They amounted to nearly 1 gram.

By cooling the fraction boiling at 200—210° under 40 mm. pressure in a freezing mixture, a white, powdery mass was obtained, which on recrystallisation from light petroleum formed colourless, prismatic crystals melting at 33—34·5°. On analysis:

0·2026 gave 0·5982 CO_2 and 0·1576 H_2O. C = 80·53; H = 8·64.

$C_{19}H_{24}O_2$ requires C = 80·28; H = 8·45 per cent.

Dipropyloxydiphenylmethane is insoluble in water, but extremely easily soluble in methyl or ethyl alcohol, ether, benzene, light petroleum, &c. It is rather unstable, the faces of crystals very soon becoming dull. Well formed crystals are very difficult to obtain.

The amount of the fraction boiling at 200—210° under 40 mm. pressure corresponds to 35 per cent. of the theoretical yield.

Diisobutyloxydiphenylmethane, $(C_6H_5)_2C[O\cdot CH_2\cdot CH(CH_3)_2]_2$.

The preparation of this substance was effected in the way previously described, the quantities taken being 3·7 grams of sodium, 41 grams of *iso*butyl alcohol, and 19 grams of benzophenone chloride. When the sodium compound melted, a brisk action took place, but was not complete after heating to 130—150° for 7 hours, the liquid still showing an alkaline reaction. The salt was removed by filtration, and the liquid then distilled under diminished pressure. After removal of the excess of *iso*butyl alcohol, the temperature rose rapidly to 199°, and 16·5 grams of a thick oil were collected, having a boiling point between 199° and 210° under 35 mm. pressure. When placed in a freezing mixture, this oil became a thick jelly in which minute needles appeared on scratching. After standing at the ordinary temperature for 18 days, the small bunches of needles, which had grown, were filtered off, dried on a porous plate, and, as they showed no sharp melting point, dissolved in ether. The ethereal solution deposited silky needles after being kept in a desiccator for a week. The dried crystals, which weighed 0·8 gram, now melted at 62—64°, but on exposure to the air the melting point fell, and, as will be shown later, the substance decomposed with the formation of benzophenone. A combustion performed a week after the separation of the crystals gave the following figures:

0·2682 gave 0·8313 CO_2 and 0·1657 H_2O. C = 84·5 ; H = 6·86.

$C_{21}H_{28}O_2$ requires C = 80·76 ; H = 8·97 per cent.

$C_{13}H_{10}O$ „ C = 85·71 ; H = 5·49 „

The quantity being so small, no experiments could be carried out to ascertain the reason for the difference in melting point between these crystals and those described below.

The oil from these crystals was again distilled under a pressure of 35 mm., when eleven grams, or 44 per cent. of the theoretical quantity obtainable, came over between 203° and 215°, mostly at 210°. By cooling in a freezing mixture, small, diamond shaped plates crystallised from the oil, which gradually became solid throughout. After drying on a porous plate, the solid melted at 36—38°, but the melting point was lowered by exposure to the air. From an ethereal solution,

crystals melting at 35—37°, and from light petroleum, crystals melting at 35—36°, were obtained.

On analysis of the crystals melting at 36—38°, the following numbers were obtained:

0·2041 gave 0·6017 CO_2 and 0·1644 H_2O. C = 80·40; H = 8·95.
0·2076 „ 0·6131 CO_2 „ 0·1669 H_2O. C = 80·54; H = 8·92.
$C_{21}H_{28}O_2$ requires C = 80·76; H = 8·97 per cent.

The following experiment is a further proof that the substance has the formula attributed to it. 0·2660 gram of the crystals in a platinum boat was placed in a desiccator over sulphuric acid and weighed every second day. The crystals soon deliquesced, then became entirely liquid, meanwhile steadily losing weight for nearly three weeks. At the end of the fourth week, the weight had become constant, and on introducing a particle of benzophenone, the reddish-brown oil crystallised. The loss in weight amounted to 0·1080 gram, or 40·6 per cent. The loss in weight caused by splitting off di*iso*butylic ether from di*iso*butyloxydiphenylmethane is 41·6 per cent. An analysis of the residual product proved it to be impure benzophenone.

0·1562 gave 0·4858 CO_2 and 0·0794 H_2O. C = 84·82; H = 5·65.
$C_{13}H_{10}O$ requires C = 85·71; H = 5·49 per cent.

In this respect, therefore, the di*iso*butyloxy-derivative agrees with the dimethoxy- and diethoxy-compounds.

Di*iso*butyloxydiphenylmethane is exceedingly soluble in the ordinary organic solvents. Although it crystallises more readily than the propyloxy-compound, it is difficult to work with in summer weather on account of its low melting point and ready dissociation.

Attempt to prepare Diamyloxydiphenylmethane.

The quantities used in this experiment were 2·8 grams of sodium, 50 grams of amyl alcohol (b. p. 129·5—130·5°), and 13·6 grams of benzophenone chloride. The mixture was heated—after a violent action had taken place—in an oil-bath to 135—145° for 5 hours. Dry ether was then added to the still alkaline product, and the solution filtered from the salt. On fractional distillation under 40 mm. pressure, 3 grams of oil boiling between 200° and 220°, 10·2 grams between 220° and 235°, and 4·3 grams between 235° and 260° were obtained. The two latter portions formed a jelly when placed in a freezing mixture, but no crystals separated. On exposure to winter cold during the Christmas vacation, small groups of stellate needles were obtained, which after drying between filter paper melted at 66—67°. Only a very small quantity was obtained, and further efforts to get more were fruitless. An analysis gave figures which

lie between those required for the amyloxy-compound and benzophenone.

0·1268 gave 0·3887 CO_2 and 0·0745 H_2O. C = 83·60 ; H = 6·53.
$C_{22}H_{32}O_2$ requires C = 81·65 ; H = 8·87 per cent.
$C_{13}H_{10}O$ „ C = 85·71 ; H = 5·49 „

4 : 4′-Dihydroxytetraphenylmethane, $(C_6H_5)_2C(C_6H_4\cdot OH)_2$.

It is curious that this compound is the product of the action of sodium phenoxide on benzophenone chloride, and that no diphenoxy-compound could be isolated. Two methods of preparation are described. In the first, sodium phenoxide was prepared by adding 4·6 grams of sodium to a solution of 18·9 grams of phenol in dry ether, long continued heating and frequent shaking being necessary to convert the sodium into sodium phenoxide (which is almost insoluble in ether) ; 23·7 grams of benzophenone chloride were then mixed with the product. On heating, no action took place until the ether was distilled off, when violent ebullition set in, vapours of phenol being evolved. The residue was heated for 1½ hours in an oil-bath at 115°, and when cold extracted with ether. The ethereal extract was repeatedly shaken with water until the washings no longer had an alkaline reaction. From the first washings, phenol separated as an oil on the addition of hydrochloric acid. After drying the ethereal extract and distilling off the ether, there remained an uninviting, thick, brown oil, which would neither solidify on cooling in a freezing mixture nor on the introduction of particles of benzophenone or phenol. After trying to crystallise it from alcohol, ether, chloroform, and other solvents, it was found that by the addition of light petroleum to the ethereal solution, small crystals separated, and after several days a product very like treacle filled the bottom of the beaker. This was spread on a porous plate and then dissolved in a large volume of chloroform and boiled under a reflux condenser with animal charcoal to decolorise it. Repeated boilings reduced the colour of the solution to a light yellow, and on the addition of light petroleum, light yellow, sandy crystals separated. After several recrystallisations, the substance softened at about 260° and melted at 285—287°.

Analysis showed that the substance had the peculiar composition of 2 molecules of ether combined with 1 of dihydroxytetraphenylmethane.*

0·1330 gave 0·3862 CO_2 and 0·0943 H_2O. C = 79·19 ; H = 7·89.
$C_{25}H_{20}O_2,2C_4H_{10}O$ requires C = 79·20 ; H = 8·00 per cent.

* Baeyer has obtained dichloral peroxide hydrate with one molecule of ether of crystallisation, $C_4H_4Cl_6O_4,C_4H_{10}O$ (*Ber.*, 1900, **34**, 2482).

The ether of crystallisation was expelled by heating in a steam oven. A portion of the substance, which had already lost in weight by standing in an exhausted desiccator for several days, lost more than 20 per cent. by heating, the theoretical loss being 29·6 per cent. The results of the analysis of a portion of the substance so obtained were:

0·1418 gave 0·4412 CO_2 and 0·0800 H_2O. C = 84·85; H = 6·26.
$C_{25}H_{20}O_2$ requires C = 85·22; H = 5·68 per cent.

The following method of preparation was found to give much better results: 6·1 grams of sodium dissolved in 130 grams of phenol and 31·6 grams of benzophenone chloride were heated in a water-bath until hydrogen chloride ceased to come off, which was at the end of 22 hours. The excess of phenol was then distilled off under 40 mm. pressure at 130—140°, and the residue, mixed with water, repeatedly extracted with ether. The ethereal solution was washed with caustic soda solution and then with water, dried, and boiled for 6 hours with animal charcoal. After filtration and concentration, the solution on cooling became almost solid. The greenish-brown, crude substance so obtained weighed 61 grams, or 91 per cent. of the theoretical quantity. After further boiling with animal charcoal and recrystallisation, the crystals melted at 284—285°.

Qualitative experiments show that benzophenone chloride and phenol react directly with production of the above product, but no quantitative experiment has yet been performed.

Dihydroxytetraphenylmethane is a colourless, crystalline substance which dissolves very easily in ether, easily in alcohol, and moderately in chloroform, but only sparingly in light petroleum. It is soluble in caustic soda without coloration, and is reprecipitated by the addition of an acid. It does not give the bromine colour reaction mentioned by Russanoff for the corresponding dihydroxytriphenylmethane.

By heating the substance with its own weight of fused sodium acetate and four times as much acetic anhydride, an acetyl derivative was obtained, which, after recrystallisation from acetone, melted at 170—171°. Analysis showed it to be the diacetyl compound.

0·2194 gave 0·6386 CO_2 and 0·1202 H_2O. C = 79·38; H = 6·08.
$C_{29}H_{24}O_4$ requires C = 79·81; H = 5·50 per cent.

Action of Ethyl Alcohol on Benzophenone.

From the easy dissociation of the above compounds, it was thought possible that they might be formed directly from benzophenone and the corresponding alcohol, but this proved not to be the case, as the following experiments showed.

Five grams of benzophenone were heated with 20 grams of ethyl

alcohol in a water-bath for 3 hours and allowed to stand overnight. No crystals having appeared, most of the alcohol was distilled off. The residual oil did not crystallise on standing, but on the addition of a particle of benzophenone, a rapid growth of crystals took place. After drying they melted at 48—49°, and were evidently unchanged benzophenone. A further crop of crystals from the mother liquor brought the amount recovered up to 4·8 grams.

Action of 1 *per cent. Solution of Hydrogen Chloride in Methyl Alcohol on Benzophenone.*

As E. Fischer (*Ber.*, 1897, 30, 3053; 1898, 31, 545, 1989) mentions that the use of 1 per cent. alcoholic solutions of hydrogen chloride is particularly adapted to the production of aldals, and only infers that it is not applicable for the production of ketals, the following experiments were performed. These show that the process is inapplicable in the case of benzophenone.

Five grams of benzophenone were dissolved in 100 c.c. of 1 per cent. solution of hydrogen chloride in methyl alcohol, and the mixture allowed to stand for 5 days. Most of the alcohol was then removed by distillation, and the residue crystallised on cooling. The crystals were separated from the mother liquor, which afforded a second crop on standing, the amount recovered being 4·9 grams. The crystals melted at 48—49° (benzophenone m. p. 48°), hence the benzophenone was unacted on.

A similar experiment in which 5 grams of benzophenone and 40 c.c. of 1·5 per cent. solution of hydrogen chloride in methyl alcohol were heated in a sealed tube at a temperature of 75—90° for 12 hours also resulted in the recovery of the whole of the benzophenone unchanged.

Dimethoxydiphenylmethane.

Action of Nitric Acid on Dimethoxydiphenylmethane.—The following experiment was performed in the hope of obtaining the nitro-derivative of dimethoxydiphenylmethane, but dissociation took place, and dinitrobenzophenone resulted.

Two grams of the powdered crystals were slowly added to 25 c.c. of fuming nitric acid cooled by ice, the crystals dissolving apparently without change. After standing for a day, the solution was poured on to crushed ice, by which means a white, curdy precipitate was formed. The weight of dried precipitate was 2·1 grams. It dissolved easily in hot ethyl alcohol, and from the solution there separated simultaneously pale yellow leaflets and needle-like crystals, neither of which showed a constant melting point. As this might be due to a

mixture of isomerides, analyses of different portions of the substance, which had been kept in desiccators until of constant weight, were made.

0·3082 gave 27·9 c.c. moist nitrogen at 13° and 757 mm. N = 10·66.
0·2287 „ 20·4 c.c. „ 13° „ 759 mm. N = 10·52
$C_{13}H_8O_5N_2$ requires N = 10·30 per cent.

As dinitrobenzophenone exists in several modifications, further efforts were made to separate the possible isomeric forms. From a fairly concentrated nitric acid solution, glistening crystals resembling sand were deposited. They melted at 189—190°, and crystallised from hot glacial acetic acid in fan-shaped groups of needles, thus agreeing with the properties of 4 : 4′-dinitrobenzophenone (Städel, *Ber.*, 1894, 27, 2110).

On heating the mother liquor from the above experiment and diluting it with hot water, a second crop of crystals consisting of rosettes and needles was obtained. Recrystallised from glacial acetic acid, they softened at 137° and melted at 149°, thus conforming with the description of the properties of 3 : 3′-dinitrobenzophenone.

Neither of these substances is appreciably volatile with steam, and both are very sparingly soluble in ether.

Diphenylmethyleneanilide, $(C_6H_5)_2C{:}N{\cdot}C_6H_5$.—This substance was formed when dimethoxydiphenylmethane was heated with three times its weight of aniline. At about 60°, the solid had all dissolved, and at 175° crystals began to separate and a slight ebullition occurred. After being kept at 180° for 5 minutes, the product was allowed to cool, filtered with the aid of a pump, and the residue washed with dry ether. From a hot methyl alcoholic solution of the residue, glistening, yellow plates separated, showing a melting point of 113—113·5°; Rohde gives 112—113° (*Ber.*, 1892, 25, 2056).

II. *Action of Sodium Alkyloxides on Benzal Chloride under the ordinary Pressure.*

*Action of Sodium Methoxide.**

According to Wicke's instructions (*Annalen*, 1857, 102, 356), 23 grams of sodium were dissolved in 250 c.c. of methyl alcohol, 80·5 grams of benzal chloride added to the solution, and the mixture heated in a water-bath for 15 hours. As it was thought possible that methyl chloride might be formed, this being the case when the action takes place under pressure, an apparatus for collecting gas was attached to

* As the products obtained in these experiments were not all of the same character, they will be described under the heading of the sodium derivative of the alcohol which acted on benzal chloride.

the end of the reflux condenser, but no gas was found to be evolved. After removing the alcohol by distillation, the residue, which was alkaline, was mixed with water, and the oil which separated extracted by ether. The ethereal extract was dried over calcium chloride, the ether removed, and the residue subjected to fractional distillation under diminished pressure. In this way, a colourless oil which distilled between 190° and 210° under the ordinary pressure was obtained.

On testing the various fractions between 190° and 210° for chlorine, it was found to be present in all. Only after heating this oil with fresh quantities of sodium methoxide in alcoholic solution several times, could it be obtained free from chlorine.

In another experiment, potassium was substituted for sodium, and zinc dust and alcoholic potash were used to remove the last traces of chlorine, as described under sodium ethoxide. In this way, 12 grams of an oil boiling between 180° and 210° were obtained free from chlorine. Supposing it to be pure dimethoxybenzylidene, this would be a yield of 15 per cent. of the theoretical.

Analysis of the portion boiling at 194—196° gave the following figures:

0·1671 gave 0·4345 CO_2 and 0·1160 H_2O. C = 70·91; H = 7·71.

$C_9H_{12}O_2$ requires C = 71·06; H = 7·89 per cent.

Dimethoxybenzylidene is a colourless, limpid oil, with an odour of geranium. It boils at 194—196°, Fischer (*Ber.*, 1898, **31**, 549) giving 198°, and Wicke 208°, as its boiling point. The last is probably incorrect, as Wicke gives no analysis, and his product probably contained unchanged benzal chloride.

Action of Sodium Ethoxide.

In this experiment, 23 grams of sodium were dissolved in 230 grams of ethyl alcohol, and to the cold solution 80·5 grams of benzal chloride were added. The mixture was heated in a water-bath for 24 hours, no violent action taking place, but salt gradually separating. At the end of this time, the liquid was still alkaline. Having distilled off most of the alcohol, the residue was mixed with water and extracted three times with ether. The ethereal solution was washed with water until it showed a neutral reaction, dried over calcium chloride, filtered, and the ether evaporated. The residue was then distilled under a pressure of 45 mm., nearly the whole coming over between 90° and 175°. On redistilling this under the ordinary pressure, 3·6 grams were collected below 206°, 59·3 grams between 206° and 220°, and 6·3 grams between 220° and 300°. As all these fractions contained chlorine, those boiling up to 220° were added to a solution of 9 grams of sodium in 100 grams of alcohol, and the mixture heated on the water-bath for 17 hours. A

separation of salt again took place, and the liquid darkened in colour. The product was treated as before, and 51·1 grams of a colourless liquid boiling at 135—140° under 75 mm. pressure were obtained, which, under the ordinary pressure, distilled between 200° and 220°. As the various fractions still contained chlorine, they were heated a third time with sodium ethoxide (4·5 grams sodium in 45 grams alcohol) for 16 hours, and subsequently treated as before. The fractions collected were: 6·2 grams at 212—215°; 13·3 grams at 215—217°; 12·6 grams at 217—219°; 4·2 grams at 219—222°. As they all still showed the presence of traces of chlorine, the action of zinc dust and alcoholic potash was tried on the two latter fractions. Sixteen grams of the oil mixed with 5 grams of potassium hydroxide dissolved in 20 grams of alcohol, diluted with water to make a solution, and 5 grams of zinc dust were allowed to stand at the ordinary temperature for five days, and then heated under a reflux condenser for an hour in a water-bath. The alcohol having been removed by distillation, the residue was mixed with water, extracted with ether, dried, and the ether expelled. The resulting product now distilled at 216° to 220°, chiefly at 217°, 13 grams being so obtained.

In order to make certain of the absence of chlorine, a Carius estimation was carried out.

0·5890 gave 0·0004 AgCl and ash. Ash = 0·0001.

It is very curious that Wicke makes no mention of the difficulty of removing the chlorine compounds in this reaction. On the other hand, Limpricht, who repeated Wicke's work, but heated the mixture of benzal chloride, sodium methoxide, and alcohol at 140°, was unable to obtain products free from chlorine, the amount of the latter varying between 7·5 and 18·7 per cent.

The absence of chlorine having been established, the liquid was once more fractionally distilled, and 7·5 grams of oil boiling at 216—217° (uncorr.)* were collected. Wicke, with whom Fischer agrees, mentions 222° as the corrected boiling point of diethoxybenzylidene. A combustion † of this portion gave the following figures:

* The temperatures throughout this investigation are uncorrected.

† The combustion of this substance was a matter of some difficulty, because, on heating it apparently splits off ethyl ether, which, if allowed to pass over rapidly, causes the percentage of carbon to come out too low. The following analyses of portions (I and II boiling at 217—219°, III at 216—220°, and IV at 216—217°) which were free, or as nearly as possible free, from chlorine illustrate this fact.

I.	0·3745 gave 0·9706 CO_2 and 0·2933 H_2O.	C = 70·68; H = 8·70.
II.	0·1690 ,, 0·4397 CO_2 ,, 0·1360 H_2O.	C = 70·90; H = 8·94.
III.	0·6398 ,, 1·6868 CO_2 ,, 0·5056 H_2O.	C = 71·93; H = 8·77.
IV.	0·5438 ,, 1·4243 CO_2 ,, 0·4255 H_2O.	C = 71·43; H = 8·67.

$C_{11}H_{16}O_2$ requires C = 73·33; H = 8·88 per cent.

In the above four analyses, the combustion was carried out at an ordinary rate, an

0·24 gave 0·645 CO_2 and 0·2 H_2O. C = 73·29 ; H = 9·25.
$C_{11}H_{16}O_2$ requires C = 73·33 ; H = 8·88 per cent.

Diethoxybenzylidene is a colourless liquid with a fragrant odour. It is not soluble in water, but is miscible with the ordinary organic solvents. It is stable in the presence of alkalis, but is readily decomposed by acids. With a saturated solution of sodium bisulphite it soon yields the benzaldehyde compound.

Assuming that the fractions 215—222°, weighing 30·1 grams in all, consisted of pure diethoxybenzylidene, the yield would be 33 per cent. of the theoretical. This is, therefore, not so convenient a method as E. Fischer's for the preparation of this substance.

Action of Sodium Benzoxide.

The quantities used in this experiment were 4·6 grams of sodium, 50 grams of benzyl alcohol, and 16·1 grams of benzal chloride. The mixture was heated in an oil-bath at a temperature of 206—210° for 5 hours, during which a quantity of solid matter separated. When cold, a large volume of ether was added and the solution filtered, the salt being washed several times with ether. After removal of the ether, the yellow oil which remained was distilled under a pressure of 55 mm., fractions being collected between 100° and 270°. The residue in the distilling flask was a viscous mass. The last fraction of distillate, namely, that boiling at 200—270°, smelt of benzaldehyde, and contained some chloride. On distillation under the ordinary pressure, the temperature steadily rose to 300°. A further effort to obtain a constant boiling liquid under a reduced pressure of 60—65 mm. was also unsuccessful, the distillate being collected in the following fractions: up to 115°, 9·3 grams ; 115—120°, 12·3 grams ; 120—195°, 11·9 grams ; 195—260°, 5·3 grams, and 260—300°, 6·8 grams. The first two fractions were found to be free from chlorine, and as they distilled at 195—202° under 749 mm. pressure, were probably benzyl alcohol (b. p. 204°). The other portions all contained chlorine. By cooling the last fraction in a freezing mixture, a small quantity of crystals separated. These were filtered off, dried on a porous plate, and then melted at 112—115°. As the presence of stilbene and benzoic acid, which both melt at 120°, was suspected, the following tests were performed. The crystals did not dissolve in solutions of either sodium hydroxide or carbonate, nor did they react with litmus,

hour to an hour and three-quarters being taken between the introduction of the substance and the removal of the absorption apparatus. In the combustion mentioned in the text, the time was extended to two hours and a half. This observation was also made by Dr. A. J. Walker when burning dimethoxybenzylidene.

but they decolorised a solution of bromine in carbon disulphide, thus indicating the absence of benzoic acid, and the presence of stilbene. They were then purified by recrystallisation from hot ethyl alcohol. The glistening leaflets, of which only a minute quantity was obtained, melted sharply at 120°, and on analysis gave the following figures:

0·0316 gave 0·1078 CO_2 and 0·0246 H_2O. C = 93·02; H = 8·65.
$C_{14}H_{12}$ requires C = 93·33; H = 6·67 per cent.

With the idea of removing any benzoic acid, and possibly chlorine compounds, from the fractions 195—260° and 260—300°, an ethereal solution of them was shaken with aqueous solutions of sodium carbonate and hydroxide, dried, and, after the removal of the ether, distilled under 85 mm. pressure. In this way, 5·5 grams were obtained, distilling between 200° and 240°. On mixing with light petroleum and cooling in a freezing mixture, there separated some crystals, which when dry weighed 0·11 gram. As they resembled the crystals of stilbene above mentioned, the bromide was prepared.

An ice-cold ethereal solution of bromine was immediately decolorised by an ethereal solution of these crystals. After standing 4 hours in the cold, the silky needles which had been deposited from the solution, were filtered off and dried on a porous plate. The weight of crystals obtained was 0·124 gram, and they melted at 236—237°. As stilbene dibromide melts at 237°, this experiment confirms the results of the analysis.

From the mother liquor of the stilbene, no liquid of constant boiling point could be isolated, and it still contained a considerable quantity of chlorine. The action of sodium benzoxide on benzal chloride would thus appear to be a rather complicated one, the formation of stilbene only taking place in very small quantity.

Action of Phenol on Benzal Chloride.

As it had been found that benzophenone chloride acted directly on phenol, the same result was expected in the case of the above substances. A mixture of 55 grams of phenol and 16·9 grams of benzal chloride was heated gently at first, then to 120° for 10 hours, when hydrogen chloride ceased to come off. The loss in weight of hydrogen chloride was 7 grams, or 95 per cent. of the theoretical. From the dark brown residue, phenol was distilled off under 50 mm. pressure at 100—107°, the temperature being allowed to rise to 210°. On removing the capillary tube from the ruby-red, transparent jelly remaining in the flask, a sharp click was heard, and crystals shot out radially from the centre. The weight of crystalline solid was 24 grams, or 87 per cent. of the theoretical. After boiling with animal charcoal and recrystallising from chloroform, the colourless crystals of dihydroxy-

triphenylmethane melted at 160—161°. As mentioned by Russanoff (*Ber.*, 1889, 22, 1944), when gently warmed with bromine water, washed, and dissolved in alcohol, this substance gives a beautiful, blue colour on the addition of caustic alkalis.

When heated with acetic anhydride and fused sodium acetate, it affords a diacetyl derivative, which crystallises from acetone in colourless crystals melting at 108—110°. In this respect, therefore, it also agrees with the product obtained by Russanoff by the condensation of benzaldehyde and phenol by means of sulphuric acid.

III. *Action of Sodium Alkyloxides on Benzal Chloride under Pressure in Sealed Tubes.*

Action of Sodium Methoxide.

In this experiment, 41·4 grams of benzal chloride were added to a solution of 6 grams of sodium in 60 grams of methyl alcohol, and the mixture heated at 100—105° for 6 hours. On the tube being opened, only a slight pressure of gas was noticed, but a considerable quantity of a white salt had separated. The tube was again sealed and heated at 150° for 3 hours; on reopening, a strong pressure of gas was observed, and the liquid contents were faintly acid to litmus. After standing for a few minutes, the liquid began apparently to boil, and methyl chloride was briskly evolved for more than an hour. It may be noted that a corresponding result was obtained with the other alcohols used under similar conditions.

The residue was filtered with the aid of the pump, and the liquid thus obtained was distilled under a pressure of 75 mm., the fractions collected being 21·7 grams below 35°, and 24 grams between 35° and 105°, chiefly 100—105°. On redistillation under the ordinary pressure, nearly 20 grams of crude methyl alcohol, boiling between 66° and 70°, and 23 grams of crude benzaldehyde, boiling between 175° and 195°, were obtained. The crude benzaldehyde so obtained corresponds to a yield of 87 per cent. of the theoretical.

From the residue, a small quantity of a crystalline acid melting at 121° was obtained (benzoic acid melts at 121°), probably formed by the oxidation of the aldehyde.

Action of Sodium Ethoxide.

This experiment was carried out in a similar manner to the previous one, the quantities taken being 4·6 grams of sodium, 47 grams of ethyl alcohol, and 32 grams of benzal chloride. The mixture was heated at 150—160° for 7 hours. No pressure of gas was noticeable on opening the tube, but on heating to 55° a large volume of gas was

liberated. The gas, which measured 2·25 litres, was collected in a gas holder. After passing it through two wash-bottles containing sulphuric acid, some of the dry gas was liquefied in U-tubes immersed in a freezing mixture. About four c.c. of the colourless, very mobile liquid which was obtained in this way evaporated very rapidly when removed from the freezing mixture. The vapour burned with a green edged flame, and was evidently ethyl chloride. The volume of gas measured was about half that which should theoretically have been obtained.

The contents of the tube were next filtered with the aid of the pump, and after distilling off the unchanged alcohol from the filtrate, the temperature was raised to 210°, the oil which came over amounting to nearly 23 grams. The residue was dark brown in colour and resembled pitch. It did not give evidence of the presence of chlorine as shown by the sodium test. On heating alone, it gave off a very acrid odour. A solution obtained by boiling it with water and filtering hot, deposited glistening leaflets, which melted at 121° (benzoic acid melts at 121°).

On redistilling the oil, the temperature rose rapidly to 175° and between 175° and 185° more than 12 grams, and between 185° and 210° 5·5 grams, came over. On shaking with a cold saturated solution of sodium bisulphite, both these fractions were shown to consist mainly of benzaldehyde, and the presence of only a small quantity of benzal chloride in the latter fraction was proved by the tests for chlorine.

Action of Sodium Propyloxide.

In this experiment, 4·6 grams of sodium, 50 grams of propyl alcohol, and 32·2 grams of benzal chloride were heated at 150° for 7 hours. No gas escaped on opening the tube. The tube was then connected with a condenser, to which two U-tubes, immersed in a freezing mixture, were attached. It was heated in the outer tube of a V. Meyer vapour density apparatus filled with water. When the temperature of the water rose to 55°, bubbles of gas began to come off, and after heating for an hour and a quarter, during which time the temperature gradually rose to 97°, all the gas seemed to have been evolved. The liquid, condensed in the U-tubes, weighing 11·4 grams, was then fractionally distilled, a Linnemann column being used. The temperature, which rose to 43° before any liquid distilled over, remained constant at 46° for some time, and then rose rapidly to 90°. The fractions collected were 43—48° (chiefly 46°), 4·4 grams; 48—97° (chiefly 90—94°), 6·4 grams. The former was a colourless, mobile, strongly refractive and pleasant smelling liquid resembling propyl chloride in all its properties (propyl chloride boils at 46·5°). A yield of 4·4 grams of propyl chloride

corresponds to 28 per cent. of the theoretical. The latter portion was chiefly propyl alcohol.

The residue in the tube was mixed with about 250 c.c. of water and extracted with ether eight times. The ethereal extract, which was neutral to litmus, was dried over calcium chloride, and, after expelling the ether, was distilled, 26 grams of a mobile liquid coming over below 105° and 18·5 grams of an oil between 175° and 230°. The first portion consisted mainly of propyl alcohol, whilst the last had a strong odour of benzaldehyde, but was found to contain a considerable quantity of chlorine. In order to get a rough estimate of the quantity of benzaldehyde present, the last portion was shaken with a saturated solution of sodium bisulphite, and the crystalline compound thus formed filtered with the aid of the pump, washed twice with ethyl alcohol, and dried on a porous plate. The weight of the dry bisulphite compound was 9·6 grams, or 23 per cent. of the theoretical.

Action of Sodium Benzoxide.

In this experiment, 4·6 grams of sodium dissolved in 50 grams of benzyl alcohol and 32 grams of benzal chloride were heated at 150—160° for 11 hours. On opening the tube, slight pressure was noticeable, a combustible vapour escaping. A small quantity of glistening leaflets, which had crystallised in the upper part of the tube, proved to be insoluble in cold, but readily soluble in hot, water, and also in caustic soda, from which they were reprecipitated by the addition of hydrochloric acid. After drying, the crystals softened at 90° and melted at 118°, agreeing generally therefore with the properties of benzoic acid. The contents of the tube were then filtered, and the oil thus obtained subjected to fractional distillation under 60 mm. pressure, the temperature being allowed to rise to 140°, at which point crystals appeared in the condenser. The fractions were then distilled under the ordinary pressure, and 7·2 grams were collected between 162° and 176°, and 20 grams between 176° and 178°. As the last fraction was expected to be benzyl chloride, chlorine estimations were made with the following results:

0·2673 gave 0·2330 AgCl. Cl = 21·5.
0·2207 „ 0·1918 „ Cl = 21·5.
C_7H_7Cl requires Cl = 28·06 per cent.

As the liquid probably contained benzaldehyde, it was shaken with a saturated solution of sodium bisulph ; the colourless crystalline substance so obtained was filtered off, and proved to be the benzaldehyde bisulphite compound. The oil was then separated by the addition of water and extraction with ether. After drying the ethereal extract and removing the ether, the residue was distilled under a pressure of

70 mm., when it came over between 100° and 110°. Unfortunately some was lost, but of the remaining 8·7 grams, 1·8 grams distilled below 176°, and 5·7 grams at 176—177° under the ordinary pressure. The latter portion showed all the properties of benzyl chloride (b. p. 179°), and a chlorine determination gave satisfactory figures.

0·2635 gave 0·2967 AgCl. Cl = 27·9.

C_7H_7Cl requires Cl = 28·06 per cent.

In another experiment, in which the same quantities were used, the components were thoroughly mixed by stirring with a glass rod before sealing off the tube. After heating at 150—155° for 11 hours, the sodium chloride which had separated was filtered off, with the aid of a pump from the brown liquid, washed with a little benzyl alcohol, and dried. It weighed almost 12 grams, the calculated quantity being 11·7 grams.

From the liquid obtained by distillation of the filtrate under 50 mm. pressure, 18·2 grams of sodium bisulphite compound were separated, corresponding to a yield of 43 per cent. of the theoretical. After repeating the distillation and treatment with sodium bisulphite, 11·8 grams of benzyl chloride, or 46 per cent. of the theoretical quantity, distilling at 175—176° under 748 mm. pressure, were obtained. An estimation of chlorine gave the following figures:

0·2165 gave 0·2403 AgCl. Cl = 27·5.

C_7H_7Cl requires Cl = 28·06 per cent.

IV. *Note on the Analysis of Benzal and Benzyl Chlorides.*

As Wicke states that the chlorine in benzal chloride is completely precipitated by the addition of an alcoholic solution of silver nitrate, it was thought that in the case of this compound and of benzyl chloride the Carius method of estimating halogens might be replaced by the more direct process. The following results, however, show that the precipitation is very incomplete in the case of benzyl chloride (I), and only partially complete in that of benzal chloride (II and III).

I. 0·3280 gave 0·3623 AgCl. Cl = 22·4.

C_7H_7Cl requires Cl = 28·06 per cent.

II. 0·6302 gave 1·0907 AgCl. Cl = 42·98.

III. 0·4226 „ 0·7314 AgCl. Cl = 42·97.

$C_7H_6Cl_2$ requires Cl = 44·09 per cent.

An attempt was also made to estimate the chlorine in benzal chloride by reduction with sodium amalgam and precipitation of the sodium chloride by silver nitrate in the usual way. The figures obtained in two experiments were:

I. 0·7012 gave 0·4654 AgCl. Cl = 16·5.
II. 1·3776 „ 0·9345 AgCl. Cl = 16·8.
$C_7H_6Cl_2$ requires Cl = 44·09 per cent.

Both the above methods were therefore inapplicable, and the Carius method had to be resorted to.

Action of Sodium Ethoxide on Ethylene Dibromide under Pressure.

A mixture of 23·5 grams of ethylene dibromide and 5·75 grams of sodium dissolved in 57·5 grams of ethyl alcohol was sealed up in a tube and, after remaining at the ordinary temperature for 2 days, during which a quantity of salt separated, was heated at 120—130° for 7 hours. On the tube being opened, a gas possessing all the properties of acetylene escaped under slight pressure. This gas burned with a brilliant, white, luminous flame, decolorised bromine water, forming oily drops having a peculiar odour, and produced a deep red and a yellowish-white precipitate in ammoniacal solutions of cuprous chloride and silver nitrate respectively, both of which were explosive when dry.

The filtrate from the salt distilled at a temperature of 68—70°, and in this way nearly all the alcohol was recovered.

The author desires to express his thanks to Dr. A. Jamieson Walker for carrying out the experiments on the action of sodium methoxide and of *iso*butyloxide on benzal chloride under the ordinary pressure. The latter, having unfortunately yielded negative results, are not recorded here.

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CXXIX.—*Action of the Chlorides of Phosphorus on Aromatic Ethers of Glycerol. Diaryloxyisopropylphosphorous Acids.*

By D. R. Boyd.

Symmetrical glycerol diphenyl ether, $OPh{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OPh$, was originally prepared by Rössing (*Ber.*, 1886, **19**, 63) from α-dichlorohydrin. Lindeman (*Ber.*, 1891, **24**, 2147) has since obtained both the diphenyl and di-*p*-tolyl ethers more conveniently by using epichlorohydrin.

These compounds appear to be the only representatives of the diaryl ethers of glycerol which have been described, and their properties have

not been very completely investigated. I recently had occasion to study the action of the chlorides of phosphorus upon the diphenyl ether, and the results obtained in this and some similar cases are recorded in the present paper.

When glycerol diphenyl ether is treated with phosphorus pentachloride, the corresponding diphenoxy*iso*propyl chloride is formed.

$$OPh\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OPh \longrightarrow OPh\cdot CH_2\cdot CHCl\cdot CH_2\cdot OPh.$$

If, on the other hand, phosphorus trichloride is used, and the product of the reaction treated with water, a large yield of diphenoxy-*iso*propylphosphorous acid is obtained.

$$CH(CH_2\cdot OPh)_2\cdot OH + PCl_3 = CH(CH_2\cdot OPh)_2\cdot O\cdot PCl_2 + HCl.$$
$$CH(CH_2\cdot OPh)_2\cdot O\cdot PCl_2 + 2H_2O = CH(CH_2\cdot OPh)_2\cdot O\cdot P(OH)_2 + 2HCl.$$

Similar results follow if glycerol phenyl *p*-tolyl ether or the di-*p*-tolyl ether is substituted for the diphenyl compound.

The behaviour of alcohols towards phosphorus trichloride has been investigated by various chemists (Wurtz, Menschutkin, Kowalewsky), who have shown that either an ester of phosphorous acid, for example, $C_2H_5\cdot O\cdot P(OH)_2$, or the corresponding chloride, $C_2H_5\cdot O\cdot PCl_2$, is formed according to the proportion of alcohol used.

More recently, Jaroschenko (*Chem. Centr.*, 1897, ii, 334) has suggested the employment of this reaction as a means of distinguishing between primary, secondary, and tertiary alcohols. According to this author, primary alcohols react with phosphorus trichloride to give phosphorus compounds of the type $R\cdot CH_2\cdot O\cdot PCl_2$, the yield in the case of *iso*butyl alcohol being 78 per cent. of the theoretical amount (compare also Kowalewsky, *Chem. Centr.*, 1897, ii, 333). Secondary alcohols, on the other hand, yield unsaturated hydrocarbons according to the equation:

$$3CH_3\cdot CH(OH)\cdot CH_3 + PCl_3 = 3CH_3\cdot CH{:}CH_2 + 3HCl + P(OH)_3,$$

the yield of propylene obtained from *iso*propyl alcohol being 80 per cent. of that required by theory.

Milobendski (*Chem. Centr.*, 1899, i, 249), however, has been unable to verify this observation in the case of *iso*propyl alcohol. He finds, on the contrary, that when phosphorus trichloride acts on this alcohol, only a very small quantity of propylene is formed, and that the main reaction proceeds according to the equation:

$$3C_3H_8O + PCl_3 = P(O\cdot C_3H_7)_2\cdot OH + C_3H_7Cl + 2HCl.$$

In view of these conflicting statements, a study of the action of phosphorus trichloride upon the glycerol diaryl ethers acquires additional interest. From the observations recorded in the present paper, it is evident that some secondary alcohols at least behave precisely in the fashion which has been recognised by Jaroschenko as characteristic

of primary alcohols. The use of phosphorus trichloride as a reagent for the recognition of the primary or secondary character of an alcohol must therefore be regarded as of very doubtful value.

The diaryloxy*iso*propylphosphorous acids here described are substances with a marked tendency to crystallise, and show a somewhat high degree of stability when compared with other derivatives of phosphorous acid of the same type already known. They undergo no change when left exposed to moist air, and can even be crystallised from boiling water. Solutions of their ammonium salts may be boiled for a long period without any decomposition taking place. The compounds, however, are quickly hydrolysed by heating with caustic potash.

Experimental.

Action of Phosphorus Pentachloride on s-*Glycerol Diphenyl Ether. Formation of Diphenoxy*isopropyl *Chloride,* $C_6H_5\cdot O\cdot CH_2\cdot CHCl\cdot CH_2\cdot O\cdot C_6H_5$.

The glycerol diphenyl ether used in this and the following experiment was prepared by Lindeman's method. It melted at 80—81°.*

Twenty-four grams of the ether (1 mol.) were mixed with 22 grams of phosphorus pentachloride (1 mol.). In a few minutes, a vigorous reaction took place, resulting in the formation of a yellow liquid. This was poured into water and heated with dilute caustic soda solution until the smell of phosphorus oxychloride had disappeared. The alkaline liquid was then extracted with ether, and the ethereal solution dried over potassium carbonate. On evaporation of the ether, an oil was obtained which was distilled under reduced pressure. The distillate, on standing, solidified. It was dissolved in light petroleum, from which, on cooling, it separated in large, transparent, oblique prisms melting at 37°. The yield was 7·5 grams, or about 30 per cent. of the theoretical amount. On analysis :

0·1534 gave 0·3862 CO_2 and 0·0848 H_2O. C = 68·66 ; H = 6·19.
0·2092 „ 0·1156 AgCl. Cl = 13·67.
$C_{15}H_{15}O_2Cl$ requires C = 68·55 ; H = 5·77 ; Cl = 13·50 per cent.

* In this connection, it may be mentioned that an unsuccessful attempt was made to prepare *as*-glycerol diphenyl ether from β-dibromohydrin. When this substance was treated with a mixture of sodium phenate and melted phenol, a satisfactory yield of a diphenyl ether was obtained, but this proved, on investigation, to be the same compound that results from α-dichlorohydrin or epichlorohydrin, namely, the symmetrical ether. This is no doubt to be explained by supposing that epibromohydrin is formed as an intermediate product by the action of the sodium phenate on the β-dibromohydrin.

The substance dissolves very easily in ether, alcohol, and other organic solvents, and in small quantity can be distilled without decomposition under the ordinary pressure.

Action of Phosphorus Trichloride on s-*Glycerol Diphenyl Ether. Formation of Diphenoxy*iso*propylphosphorous Acid.*

$CH(CH_2{\cdot}O{\cdot}C_6H_5)_2{\cdot}O{\cdot}P(OH)_2$.

In each experiment, 13 grams (3 mols.) of the diphenyl ether and 9 grams of phosphorus trichloride (4 mols.) were used. The mixture was heated in the water-bath for about half-an-hour until no more hydrogen chloride was evolved. The resulting colourless liquid, consisting of the chloride of diphenoxy*iso*propylphosphorous acid, together with the excess of phosphorus trichloride, was cooled and then poured into a litre of ice-cold water.

A somewhat vigorous reaction took place, with liberation of hydrochloric acid. After stirring for a short time, a white, viscous mass was obtained, which, on standing, became solid. In the first experiments, this product was extracted repeatedly with boiling light petroleum, in which the unchanged glycerol diphenyl ether dissolves, whilst the phosphorous acid is practically insoluble. It was afterwards found that a much more convenient method, and one giving a pure product, consists in treating the above-mentioned viscous mass at once with a considerable volume of dilute ammonia solution. On standing some hours, the whole of the diphenoxy*iso*propylphosphorous acid dissolves, leaving behind any unchanged glycerol ether. In this operation, it is necessary to use a rather large quantity of water, as otherwise the ammonium chloride which is formed, if any phosphorus trichloride should have escaped decomposition in the previous treatment with water, causes precipitation of ammonium diphenoxy*iso*propylphosphite.

On acidifying the ammoniacal solution with hydrochloric acid, an oily precipitate of diphenoxy*iso*propylphosphorous acid was obtained, which soon changed to a crystalline mass. This was filtered off, and washed well with water containing some hydrochloric acid. The washed product was dried at 100° and crystallised from ethyl acetate, from which it separated in beautiful, prismatic needles, or radiating groups of these, melting at 119—120°. The yield was 9 grams, or about 55 per cent. of the theoretical amount. On analysis:

0·1839 gave 0·3923 CO_2 and 0·0928 H_2O. C = 58·18; H = 5·66.
0·6867 „ 0·2535 $Mg_2P_2O_7$. P = 10·28.
$C_{15}H_{17}O_5P$ requires C = 58·40; H = 5·57; P = 10·06 per cent.

Diphenoxy*iso*propylphosphorous acid is slightly soluble in cold

water, giving a liquid with a faint acid reaction; from this solution, it is reprecipitated on addition of a little hydrochloric acid.* It is moderately soluble in boiling water, and, on cooling the solution slowly, separates in well-developed, prismatic needles similar to those obtained from ethyl acetate. It is very easily soluble in dilute aqueous ammonia, and if to a concentrated solution some ammonium chloride is added, the ammonium salt of the diphenoxy*iso*propylphosphorous acid is immediately precipitated in the form of an oil. This oil dissolves at once on addition of more water, and no hydrolysis occurs, even on prolonged boiling of the solution.

The acid is also readily soluble in cold caustic soda solution, but on boiling the solution quickly becomes turbid from separation of the glycerol diphenyl ether. The liquid now contains phosphorous acid, and after acidification and subsequent filtration is found to reduce mercuric chloride solution.

The substance dissolves very easily in alcohol, and somewhat less so in benzene, chloroform, acetone, or hot ethyl acetate. It is insoluble in ether, if free from alcohol, or in light petroleum.

Glycerol Phenyl p-*Tolyl Ether*, $C_6H_5\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot C_6H_4\cdot CH_3$.

This substance was obtained by an adaptation of Lindeman's method for the preparation of the symmetrical ethers.

A solution of *p*-cresol and sodium ethoxide in alcohol was treated with the theoretical amount of glycidol phenyl ether, and the mixture boiled for some hours in a reflux apparatus. The product was then cooled, poured into water, and the resulting solid precipitate washed with water, dried, and crystallised from alcohol. It formed white leaflets, which after several crystallisations melted at 73·5—76°. Repeated crystallisation did not alter the melting point. The sample analysed was obtained by hydrolysis of its phosphorous acid and subsequent crystallisation.

0·2071 gave 0·5636 CO_2 and 0·1323 H_2O. C = 74·22; H = 7·16.
$C_{16}H_{18}O_3$ requires C = 74·37; H = 7·04 per cent.

In properties, the substance closely resembles the diphenyl and di-*p*-tolyl ethers already described. It can be distilled under reduced pressure without decomposition, and may be crystallised conveniently either from alcohol or light petroleum.

* Autenrieth (*Ber.*, 1897, **30**, 2371) draws attention to the same phenomenon in the case of acids of the type of diphenylphosphoric acid, and Wurtz (*Annalen*, 1846, **58**, 75) records a similar behaviour on the part of amylphosphorous acid.

Phenoxy-p-*tolyloxy*isopropyl *Chloride*,
$C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}CH_3$.

Molecular proportions of glycerol phenyl *p*-tolyl ether and phosphorus pentachloride were mixed and the product of the reaction treated exactly as in the case of the preparation of diphenoxy*iso*propyl chloride. The substance crystallised from light petroleum in clusters of transparent plates of well-defined form melting at 60°. On analysis :

0·1624 gave 0·4130 CO_2 and 0·0895 H_2O. C = 69·36 ; H = 6·18.
0·2075 „ 0·1055 AgCl. Cl = 12·57.
$C_{16}H_{17}O_2Cl$ requires C = 69·41 ; H = 6·27 ; Cl = 12·82 per cent.

In solubility, volatility, &c., the substance closely resembles the corresponding diphenoxy-compound.

Phenoxy-p-*tolyloxy*isopropylphosphorous *Acid*,
$CH_3{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH(CH_2{\cdot}O{\cdot}C_6H_5){\cdot}O{\cdot}P(OH)_2$.

Twenty grams of glycerol phenyl *p*-tolyl ether were heated with 16 grams of phosphorus trichloride and the product treated as in the case of the diphenyl compound. The substance crystallised from ethyl acetate in radiating clusters of needles very similar to those formed by the diphenoxy-derivative, and melted at 106—107°. The yield was 16 grams, or about 65 per cent. of the theoretical quantity. On analysis :

0·1991 gave 0·4339 CO_2 and 0·1087 H_2O. C = 59·44 ; H = 6·12.
0·5528 „ 0·1945 $Mg_2P_2O_7$. P = 9·79.
$C_{16}H_{19}O_5P$ requires C = 59·59 ; H = 5·96 ; P = 9·60 per cent.

In solubility and general properties, the substance is very similar to the corresponding diphenoxy-compound. Its ammonium salt, which was obtained in the form of silky crystals, is very soluble in water and is precipitated from a concentrated solution on the addition of ammonium chloride.

Di-p-*tolyloxy*isopropyl *Chloride*,
$CH_3{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}CH_3$.

The glycerol di-*p*-tolyl ether used in the two following experiments was prepared from epichlorohydrin and *p*-cresol (Lindeman, *loc. cit.*). It melted at 88°. The ditolyl ether and phosphorus pentachloride were mixed in molecular proportion, the containing vessel being immersed in cold water in order to moderate the vigour of the reaction. The resulting liquid was treated with hot caustic soda solution and then extracted with ether as in the previous cases. On evaporation of the

ether, the residue solidified. Distillation in a vacuum was therefore omitted and the substance crystallised at once from light petroleum. It separated in small but well-developed, transparent rhombohedra melting at 70°.

0·1665 gave 0·0814 AgCl. Cl = 12·09.

$C_{17}H_{19}O_2Cl$ requires Cl = 12·19 per cent.

The properties of this substance are exceedingly similar to those of the diaryloxy*iso*propyl chlorides already described.

Di-p-tolyloxyisopropylphosphorous Acid,
$CH(CH_2{\cdot}O{\cdot}C_6H_4{\cdot}CH_3)_2{\cdot}O{\cdot}P(OH)_2$.

This substance was prepared in a manner quite analogous to that employed in the two previous corresponding cases. It crystallised from ethyl acetate in a very similar fashion, the crystals melting at 111—112°. On analysis:

0·4712 gave 0·1597 $Mg_2P_2O_7$. P = 9·43.

$C_{17}H_{21}O_5P$ requires P = 9·23 per cent.

In general properties, this substance resembles its two lower homologues very closely. It is precipitated from its aqueous solution on addition of hydrochloric acid, and its ammonium salt is precipitated on addition of ammonium chloride.

The study of these and some allied compounds is being continued.

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CXXX.—*Autofermentation and Liquefaction of Pressed Yeast.*

By ARTHUR HARDEN and SYDNEY ROWLAND.

IF a sample of washed and pressed yeast be kept in an open vessel, it will, in course of time, be observed to become darker in colour, and to change its dry, powdery condition, until, passing through all stages of pastiness, it finally becomes a thick liquid.

In the course of a series of experiments on *expressed yeast juice*, it was found advisable to study this phenomenon, especially with regard to the influence of temperature upon it and upon the accompanying phenomena of evolution of carbon dioxide and absorption of oxygen, points which have not hitherto received attention from the authors

who have described the liquefaction of yeast, or have studied the absorption of oxygen and evolution of carbon dioxide by yeast suspended in water.

Preparation of Yeast.—The yeast employed in the following experiments was top yeast obtained from an English brewery. It was freed from wort by means of a small filter press, and washed with water until the washings were quite colourless. The pasty mass was then removed from the filter press and submitted to pressure in a hydraulic press. In this way, the yeast was obtained as a friable, white mass, containing about 30 per cent. of solid matter at 100°, and capable of being crumbled between the fingers.

Influence of Temperature on Rate of Liquefaction (*Autoplasmolysis*).—The rapidity with which liquefaction is accomplished varies greatly with the temperature, and also depends on the condition of the yeast, the length of time for which it has been kept, and the temperature to which it has been exposed. The following numbers apply to a sample of yeast which was skimmed on February 15th, washed and pressed on February 19th, and then at once employed for the experiment. In this case, liquefaction at the ordinary temperature was delayed for more than two weeks, whilst at 50° it occurred within so short a time as 1—1½ hours, intermediate times being required at 26° and 39°.

Temperature.	Time of liquefaction.
14°	16 days.
26	53 hours.
39	5 ,,
50	1·25 hours.

These experiments were carried out in an atmosphere of carbon dioxide, so as to avoid any complication due to absorption of oxygen and consequent rise of temperature (see p. 1231).

Evolution of Carbon Dioxide (*Autofermentation of Glycogen*).—When yeast is preserved, the glycogen which is present in the cells gradually undergoes fermentation with production of carbon dioxide and alcohol. This phenomenon occurs both in the presence and in the absence of air, but in the former case it is accompanied by an oxidation process in which oxygen is absorbed. In order to ascertain the influence of temperature on the evolution of carbon dioxide alone, and to measure the extent of this evolution, the yeast was examined in an atmosphere of carbon dioxide or nitrogen, the nature of the indifferent gas being found to be immaterial. For this purpose, the washed and pressed yeast was rubbed into a fine powder and placed in a flask closed by an indiarubber stopper carrying two tubes, through which a current of carbon dioxide was passed to displace the air. The flask was then placed in an incubator at the desired temperature and connected with

an apparatus for collecting and measuring the evolved gases. This consisted simply of a bottle containing brine covered with a layer of oil, and connected by a syphon tube with a second graduated bottle, in which the brine displaced by the gas was collected and measured at regular intervals of time. The following table and the curves on p. 1230 show the characteristic results thus obtained at four different temperatures (50°, 39°, 26°, and 14°) with equal portions of a sample of yeast which contained 31·45 per cent. of solid matter at 100°. One hundred grams of yeast were taken in each case, and the gas was measured at atmospheric temperature and pressure over brine.

Table showing the rate of evolution of carbon dioxide by yeast exposed to different temperatures in an indifferent atmosphere. The time of liquefaction is shown by the larger type.

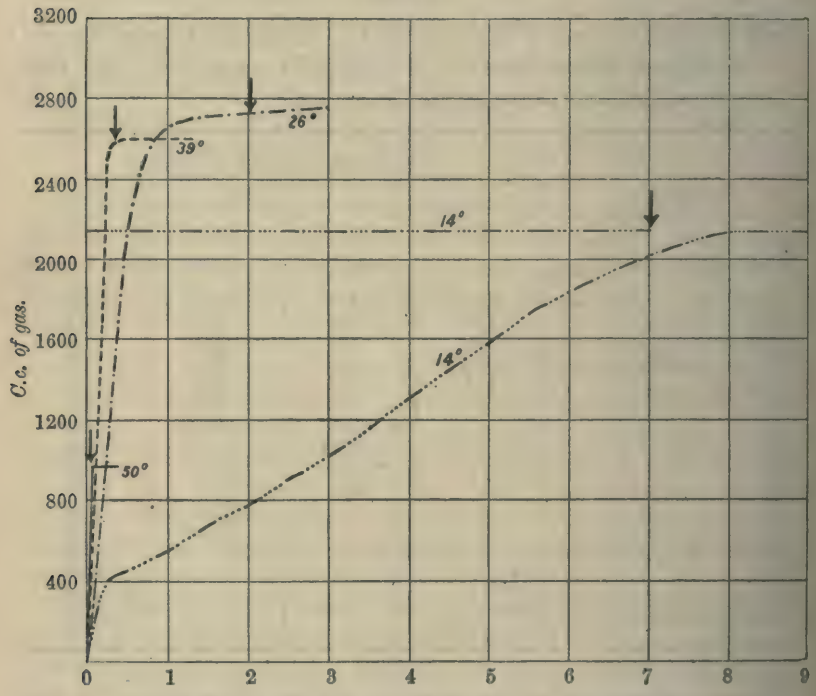
Time.	C.c. of carbon dioxide evolved at			
	50°.	39°.	26°.	14°.
20 minutes	190	110	90	80
40 ,,	450	210	165	115
1 hour	790	330	225	140
1 ,, 20 minutes	**950**	475	290	170
2 hours	950	905	400	210
3 ,,	960	1880	530	250
4 ,,		2280	680	275
5 ,,		**2400**	1505	390
22 ,,		2590	2500	530
30 ,,		2590	2695	610
48 ,,			**2720**	775
60 ,,			2730	880
96 ,,				1320
144 ,,				1840
192 ,,				2128
16 days				**2128**

These numbers and curves show, in the first place, that at 50° the evolution of carbon dioxide commences with great rapidity, but is suddenly interrupted by the liquefaction of the yeast, although microscopical examination reveals the presence of abundance of glycogen in the cells. In the three other cases, however, the total volume of gas evolved does not differ very greatly, although there is a great difference between the rates at which it is evolved. The maximum volume is produced at 26°, and amounts to 2730 c.c., which corresponds to about 5·3 per cent. of the weight of the pressed yeast, or 16·8 per cent. of the dry yeast present. It is to be noted that the evolution of gas ceases some time before liquefaction occurs. At 39°, the rate of

evolution is considerably greater, but the total volume is slightly less, the shape of the curve suggesting that in this case, as at 50°, the autofermentation is interrupted by the liquefaction of the mass. At 14°, the rate of evolution is extremely slow, and the total volume only about 75 per cent. of that evolved at 26°. This may possibly be due to the gradual exhaustion of the fermentative power of the cells.

In every case, the yeast after liquefaction was capable of growth in wort, although the samples which had been exposed to the higher temperatures commenced to develop only after a considerable time.

CURVE I.



Time in days. The arrowhead shows time of liquefaction.

It will be noted that the processes of liquefaction and evolution of carbon dioxide are interdependent in so far as evolution of gas never proceeds after liquefaction has occurred, although, on the other hand, the cessation of gas evolution does not necessarily imply immediate liquefaction.

Relation of Alcohol to Carbon Dioxide produced by Autofermentation of Glycogen.—The production of carbon dioxide by yeast kept in an atmosphere free from oxygen appears to be due to a true alcoholic fermentation, inasmuch as alcohol is produced in the characteristic

proportion to the carbon dioxide. Thus 100 grams of yeast containing 31·7 per cent. of solid matter gave, at 37°, 2160 c.c. of carbon dioxide at 18° and 766·5 mm. pressure, or 4·01 grams, together with 3·61 grams of alcohol, allowance being made for the amount of alcohol originally present in the yeast. Hence the ratio of alcohol to carbon dioxide is 1 : 1·1, which agrees closely with the ratio usually found in the ordinary alcoholic fermentation, namely, 1 : 0·96. The slight deficit of alcohol is probably due to the over-estimation of the original alcohol of the yeast, which would include the amount formed during the heating up of the water with which it was distilled.

Absorption of Oxygen.—The fact that yeast when exposed to the air absorbs oxygen is a well-established one, and the relation of this phenomenon to the production of carbon dioxide by autofermentation has been studied by Schützenberger ("Les Fermentations"), and by Gréhant and Quinquaud (*Ann. sc. nat. Botanique*, 1889, p. 269, quoted by Duclaux, *Traité de Microbiologie*, 3, 231), who examined the yeast suspended in pure water. The general result of these researches was that the amount of oxygen absorbed increases with the temperature, the maximum obtained being 9·6 c.c. per gram of dry yeast per hour at 50°. The ratio of carbon dioxide to oxygen (respiratory quotient) was also found by Gréhant and Quinquaud to increase from 1·06 at 14° to 4·5 at 46°.

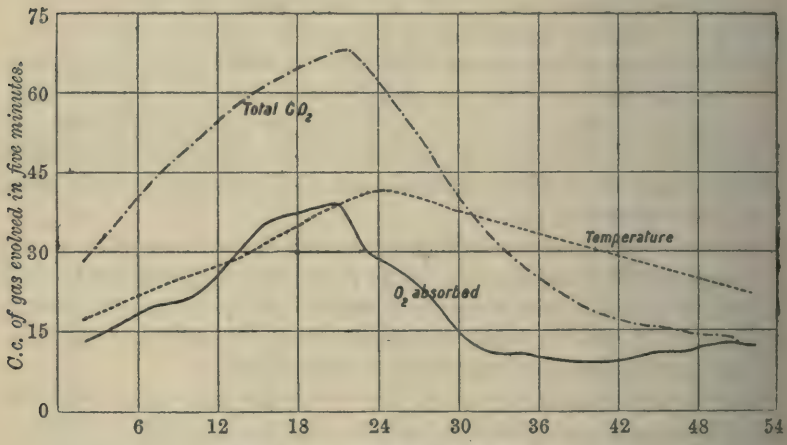
As these experiments had all been carried out with yeast suspended in water, it was thought advisable to re-examine the phenomenon as it occurs in pressed yeast, since in this condition each cell is entirely dependent on the material contained within its walls, and complications due to alimentary functions are eliminated.

For this purpose, a current of air or oxygen was passed over the yeast at a known uniform rate, and the resulting mixture of gases was collected at equal intervals of time, measured, and then passed through potash and again measured. A record was thus obtained for successive equal intervals of (1) the volume of oxygen supplied, (2) the carbon dioxide evolved, and (3) the oxygen absorbed. In order to effect this, oxygen was maintained at a constant pressure by means of a hydrostatically balanced valve in a gas-holder containing dilute caustic soda solution. The gas was then pumped through the yeast, contained in a glass cylinder, by means of two oscillating glass cylinders working in mercury, from which the gas was alternately discharged to the yeast and admitted from the reservoir, constancy of direction in the stream of gas being attained by a three-way tap changed over at the end of stroke by a gravity trip gear. The varying pressure of the brine column contained in the collecting vessel was counterbalanced by means of a mercury valve arranged in such a manner that the pressure on the gas in the delivery tube of the pump remained constant,

so that each stroke of the pump delivered exactly the same volume of gas.

Under these circumstances, the phenomena observed were of the same general character as those described by previous observers. It was found almost impossible to keep the temperature of the yeast constant during the course of such an experiment, owing to the large amount of heat evolved by the oxidation process, and in most cases, therefore, no attempt was made to do this, but the rise of temperature was observed by a thermometer inserted in the mass of yeast. In a current of nitrogen at the temperature of the air, on the other hand, no rise of temperature was observable, the autofermentation of the glycogen being very slow at this temperature and there being no oxidation, to which the rise appears to be mainly due.

CURVE II.



Equal times; periods of five minutes.

NOTE.—*In the case of the curve showing the temperature effect, the ordinates represent degrees of temperature.*

The typical course of such an experiment, carried out with freshly pressed yeast in a current of oxygen, is shown by the accompanying curve (Curve II), which applies to 69·1 grams of yeast containing 27 per cent. of solid matter.

The temperature gradually rose from 16·5° to 41·35°, and then slowly fell to 22·45°, at which point the experiment was discontinued, 4·6 hours after its commencement. During this time, 1103 c.c. of oxygen were absorbed and 2148 c.c. of carbon dioxide evolved, this being an average of 3·47 c.c. of oxygen and 6·76 c.c. of carbon dioxide per gram of fresh yeast per hour, or 12·85 c.c. of oxygen and 25·03 c.c. of carbon dioxide per gram of dry yeast per hour. This amount of oxygen, which represents the average of the whole experiment, is con-

siderably greater than the maximum amount observed by Schützenberger, which amounted to 9·6 c.c. and was observed at 50°. The respiratory quotient was 2·25 at the highest temperature observed, and gradually fell to 1, the average being 1·94.

The great ease with which gases penetrate the cell walls of yeast in this condition and come into equilibrium with the cell contents is illustrated by a phenomenon which was observed during these experiments. When yeast is allowed to stand for a short time, the cell contents become saturated with carbon dioxide. If now a measured volume of some indifferent gas be passed in, the partial pressure of the carbon dioxide being thus lowered, a large amount of the dissolved gas is at once liberated, so that there appears to be a sudden evolution of gas. Thus on passing 51 c.c. of nitrogen into 87 grams of pressed yeast contained in a cylinder connected to two gas burettes, no less than 90 c.c. of gas were at once obtained. When the yeast has been freed from carbon dioxide by a current of air or nitrogen, and carbon dioxide is then passed in, a very rapid absorption occurs, and in two or three minutes the yeast is again saturated.

As the autofermentation of the glycogen in the absence of air had been found to correspond with normal alcoholic fermentation, a comparison was instituted between the amount of carbon dioxide evolved in the presence of oxygen and in its absence, in order to obtain, if possible, some information as to the chemical action of the oxygen.

(1) One hundred grams of fresh yeast at 39° in absence of oxygen gave 1730 c.c. of carbon dioxide.

One hundred grams of the same sample in a current of oxygen at 39° gave 2090 c.c. of carbon dioxide, 844 c.c. of oxygen being absorbed. Ratio of excess of carbon dioxide evolved in presence of oxygen to the oxygen absorbed $= \frac{2090 - 1730}{844} = 0{\cdot}43.$

(2) One hundred grams of fresh yeast at 39° in absence of oxygen gave 2160 c.c. of carbon dioxide, and in a current of oxygen gave 2370 c.c. of carbon dioxide, 635 c.c. of oxygen being absorbed. Ratio of excess of carbon dioxide to oxygen absorbed $= \frac{2370 - 2160}{635} = 0{\cdot}33.$

If the oxygen oxidised the glycogen completely to carbon dioxide and water according to the equation

$$C_6H_{10}O_5 + 6O_2 = 6CO_2 + 5H_2O,$$

the amount of carbon dioxide evolved by the oxidation process would be three times that evolved by the normal fermentation process from the same weight of glycogen according to the equation

$$C_6H_{10}O_5 + H_2O = 2CO_2 + 2C_2H_6O,$$

and hence the difference between the volumes of carbon dioxide

evolved in presence, and in absence, of oxygen should be two-thirds of the volume of the oxygen absorbed.

As, however, the ratio of excess of carbon dioxide to oxygen absorbed was invariably found to be considerably less than two-thirds, it appears probable that carbon dioxide and water are not the sole products of the oxidation. This point, however, requires further investigation.

In view of the large amount of carbon dioxide evolved by yeast when it is exposed to a current of oxygen, an experiment was made to ascertain the limit of this evolution.

Twenty-five grams of yeast, containing 31·1 per cent. of solid matter, were exposed to a current of oxygen at the temperature of the air, and the carbon dioxide absorbed in caustic potash and weighed. In 12 days, 3·7422 grams of carbon dioxide were collected, so that 1 gram of dry yeast gave 0·4812 gram of carbon dioxide = 0·131 gram of carbon. Since dry yeast contains about 50 per cent. of carbon, it follows that in this case 26 per cent. of the carbon of the yeast was evolved as carbon dioxide.

Microscopical Appearance.—Coincident with the series of changes culminating in the liquefaction of the yeast, the following series of structural changes was observed microscopically. The freshly pressed yeast consists of large cells, with a small vacuole and granular protoplasm, staining a deep brown with iodine. As the evolution of carbon dioxide proceeds, the vacuole increases in size, the brown stain obtained with iodine diminishes, and just before liquefaction there is usually no glycogen left in the cell.

After liquefaction, the cells have no vacuole and are shrunken, the cell walls being crumpled and the cell substance highly granulated and contracted to a centrally aggregated mass, floating in a small amount of a clear fluid. No brown reaction with iodine is, as a rule, obtainable, and although in the case of yeast liquefied at 50°, the brown stain is obtained, the cell does not in other respects differ from the normal character.

It therefore seems probable that the liquefaction of the yeast is due to the discharge of the contents of the vacuole, and that the progressive increase in the size of the vacuole results from the accumulation of some substance produced along with carbon dioxide from the glycogen.

O'Sullivan and Tompson (Trans., 1890, 57, 872) have described the liquefaction of yeast, but did not attribute the liquefaction of the mass to the discharge of the vacuolar fluid. On the contrary, they state that "A microscopical examination at this stage shows that the yeast cells have shrivelled up into a comparatively small bulk, whilst their outline is irregular and ill-defined. The cell wall has almost entirely disappeared, but the large majority of the cells are unbroken. The vacuole occupies practically the whole of the interior of the cell,

and the granulations are very marked, being, in fact, by far the most distinct feature of it." In all the numerous samples which have come under our observation, however, the phenomenon occurs as we have described it above, and the whole progress of the change, terminating in the extrusion of the contents of the vacuole has been watched on the hot stage. The cell wall, moreover, can be quite readily distinguished throughout the process.

Our thanks are due to Mr. W. J. Young for some assistance in the experimental portion of the work.

Jenner Institute of Preventive Medicine.

CXXXI.—*Non-existence of the so-called Suboxide of Phosphorus. Part II.*

By Charles Hutchens Burgess and David Leonard Chapman.

In a previous paper (Chapman and Lidbury, Trans., 1899, **75**, 973), it was claimed: firstly, that the grounds adduced by previous investigators for the existence of a definite suboxide of phosphorus having the formula P_4O are insufficient; secondly, that the so-called suboxide of phosphorus, prepared by their methods, has properties identical with those of red phosphorus; thirdly, that when the substance is carefully purified and analysed, the percentage of phosphorus is invariably higher than that required by the formula.

Amongst the several "suboxides" prepared and examined by us was one recently obtained by Michaelis and Pitsch (*Ber.*, 1899, **32**, 337) by precipitating the red solution which results from the action of aqueous alcoholic potash on white phosphorus, with dilute hydrochloric acid. The percentage of phosphorus found by us in the substance was 90·5, which is 2 per cent. higher than that required by the formula P_4O, and in its properties the "suboxide" resembled the other preparations. A complete account of the experiments of Michaelis and Pitsch did not appear until several months after their first publication on the subject (*Annalen*, 1899, **310**, 45). In this paper, the authors lay claim to having prepared a substance free from hydrogen and other impurities, and containing the theoretical percentage of phosphorus required by the formula P_4O. It is moreover supposed to differ from amorphous phosphorus in its behaviour towards aqueous alcoholic potash.

In the present communication, we shall explain why Michaelis and

Pitsch's results cannot, in our opinion, be regarded as proof of their conclusions, and shall describe experiments which confirm the views already expressed by Chapman and Lidbury.*

The Composition of the so-called Suboxide.

Our analyses show: firstly, that the percentage of phosphorus in the "suboxide" prepared by Michaelis and Pitsch's method varies from 86 per cent. to 93 per cent.; secondly, that hydrogen is always present in considerable quantity; thirdly, that other impurities, amongst which is carbon, are also present. The explanation of the striking difference between these results and those of Michaelis and Pitsch is, we believe, to be found in the method of analysis employed by them to estimate the hydrogen. In the first place, the substance was gently heated before the analysis for hydrogen was made, in order to drive off the water which they and previous observers had found to be present. The authors evidently regard this moisture, the presence of which was directly proved by heating with copper oxide, as entirely derived from the atmosphere during manipulation, but if this view as to its source is incorrect, then the process of heating can only result in removing before analysis part of the water which it is their object to find. Some idea may be gained as to the rate at which moisture is absorbed from the air from the following experiment. 0·5946 gram of the substance was introduced into an open, wide-mouthed tube, and the rate of increase in weight observed. In 10 minutes it gained 0·0006 gram, in 35 minutes 0·0014 gram, and in 135 minutes 0·0036 gram.

Another point in connection with their experiment deserves attention. The hydrogen in the previously warmed suboxide was estimated by heating it with lead oxide in a combustion tube, and driving the resulting water by means of a current of dry air into a weighed calcium chloride tube. During the heating of the mixture of suboxide and lead oxide, a cloud was formed, which was so difficult to control that it could not be prevented from entering the calcium chloride tube. If the cloud were due to phosphorus pentoxide, and this does not seem unlikely, it would, unless the utmost precautions were taken to cause it to combine with the lead oxide, retain a large proportion of the water in the combustion tube. Again, there is no mention of the lead oxide having been heated while the current of dry air was drawn through, a precaution which certainly seems necessary.

By carefully washing and drying the substance, prepared with all the precautions given by Michaelis and Pitsch, Chapman and Lidbury

* Michaelis and Arend (*Annalen*, 1901, **314**, 259) have recently published a paper on the same subject, to which we shall also have occasion to refer later.

found that the phosphorus exceeded by 2—3 per cent. that required by the formula P_4O. Michaelis and Arend, in reply, state that the solution should be cooled to 0°, and the precipitation of the red solution effected with acetic in the place of hydrochloric acid, and that under these circumstances the substance will not contain an excess of phosphorus. From our point of view, the acetic acid is only another possible source of impurity, and it is not at all surprising that the percentage of phosphorus should have been by this means reduced. We have in the present research made no serious attempt to free the red phosphorus from this impurity, but we have simply adopted Michaelis and Arend's method of preparation, and shown by analysis that the substance obtained cannot have the formula P_4O.

Estimation of the Phosphorus in the so-called Suboxide.—The specimen was weighed out into a Geissler flask, and dissolved in a small quantity of dilute nitric acid by warming on the water-bath. As soon as the solution was complete, strong nitric acid was allowed to flow down the condensing tube together with a few c.c. of hydrochloric acid, and the mixture heated on the water-bath for 12 hours. The contents of the flask were then washed out into a large porcelain basin, and the excess of acid evaporated off. In order to be quite certain that no error was introduced from the action of the acid on the glass, the phosphoric acid was first precipitated with ammonium molybdate. The ammonium magnesium phosphate obtained from this in the usual way was dissolved in hydrochloric acid, and reprecipitated by the very slow addition of ammonia from a burette with constant stirring, 10 c.c. of magnesia mixture being added before the whole was left to stand.

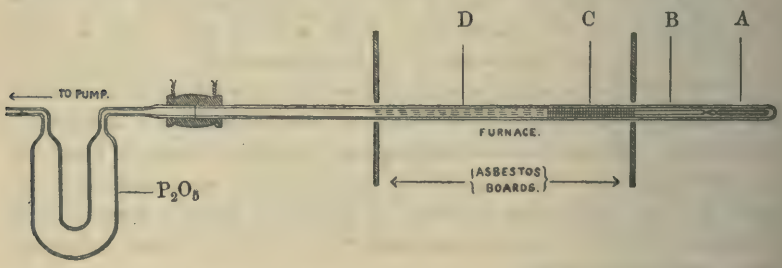
Estimation of the Hydrogen in the so-called Suboxide.—The method employed consists in distilling the specimen, whereby phosphorus vapour, steam, hydrogen, and phosphoretted hydrogen are formed. The phosphorus vapour is made to combine with copper, and the water is decomposed by red hot aluminium, so that it is thus possible to obtain all the hydrogen as gas. To avoid the absorption of moisture during manipulation, a soft glass tube, *B*, was closed at one



end, and another tube, *A*, was ground into the other end. *A* was drawn out to a fine capillary which communicated with the air. The specimen can be kept for days in such a bottle without any appreciable alteration in weight. The weighing bottle was dried in an air-bath, the "suboxide" rapidly introduced, and the stopper, *A*, inserted, the weight of the bottle having been previously obtained. After finding

the weight of the specimen, the hydrogen was estimated in the following manner:—

A hard, Jena glass tube of 8 mm. internal diameter was closed at one end, and the bottle, *A*, which contained "suboxide," dropped to the bottom. A glass rod, *B*, was then introduced, and about one-half of the remainder of the tube was first tightly packed with clean copper gauze, *C*, and then with rolls of aluminium foil, *D*. The surface of the aluminium foil had been previously cleaned by warming with ether for many hours. The Jena tube was fixed in a horizontal position, and communicated through a phosphoric oxide tube with a continuous Sprengel pump. It was thus left, with the pump working, until a good vacuum had been obtained. The part of the tube containing the copper and aluminium was then heated to a temperature at which the aluminium just began to melt. A carefully chosen tube will stand the pressure of an atmosphere at this temperature. During this heating, a little gas was pumped out from the aluminium and copper, but the volume rapidly diminished, and was soon



negligible. On heating that part of the combustion tube which contained the "suboxide" with a Bunsen burner, hydrogen was evolved in considerable quantity, and continued to come off until all the phosphorus had volatilised. The gas was collected at the pump, and retained for analysis. The residue remaining in the bottle, which contained the suboxide, was a perfectly black, non-volatile substance, and was proved to contain both carbon and phosphorus.* In two experiments, the substance was heated in the same way as described above, with the exception that no copper or aluminium was introduced into the combustion tube. The amounts of hydrogen were in these cases also far too large to allow of the substance having the formula P_4O.

Examination of the Gas Evolved.—The samples of gas which had been collected at the pump were transferred to a eudiometer and exploded with

* This residue will not burn in oxygen even when strongly heated. In one experiment, it was shown to contain carbon by heating it with lead chromate in a combustion tube and collecting the carbon dioxide in potash.

excess of oxygen. In several cases, the contraction occurring was too large for pure hydrogen. This was apparently due to the presence of some hydrocarbon, since the gas remaining after explosion was in these cases partly absorbed by potash. The improbability that the substance examined is the oxide P_4O is just as great whether the gas contained a hydrocarbon or consisted of pure hydrogen.

Preparation of the Samples.—Sample I was prepared by precipitating the red solution which results from the action of aqueous alcoholic potash on white phosphorus with very dilute hydrochloric acid. The details given by Michaelis and Pitsch (*Annalen*, 1899, 310, 56) were observed, the only variation being that the hydrochloric acid was kept in constant rotation by means of an automatic stirring apparatus. After allowing one quantity of the red solution to pass through the filter paper, the hydrochloric acid was left to stand for some time, in order to regain the temperature of the laboratory, before another quantity was prepared and filtered. As only a small amount of the substance was prepared and the time taken in its preparation was considerable, we are inclined to think that the low percentage of phosphorus is due to the action of the caustic alkali on the filter paper. The washing and drying were performed as described by Michaelis and Pitsch. The complete analysis shows that the substance cannot be a suboxide, P_4O.

Sample II was prepared without employing filter paper. The clear red solution was allowed to run from a separating funnel, drop by drop, into very dilute hydrochloric acid, which was kept stirred as before. The acid was cooled from time to time with cold water. The precipitate was washed successively with water, alcohol, and ether, and then with carbon disulphide, which has been shown to remove ordinary phosphorus completely from such a preparation (Chapman and Lidbury, *loc. cit.*, p. 976), should it happen to contain any. It will be seen from the analytical numbers that the amount of phosphorus is 4·3 per cent. higher than that required by the formula P_4O, also that the black residue left on distillation in a vacuum is much smaller than in sample I. The sample was completely soluble in aqueous alcoholic potash.

Sample III was prepared exactly according to the new directions given by Michaelis and Arend (*loc. cit.*, p. 263), the utmost precautions being taken to keep both the red solution and the precipitating acid at 0°. The red solution was prepared from sample IV. The percentage of phosphorus is still 1·5 per cent. higher than that required by the formula P_4O.

Sample IV was prepared from ammonium hypophosphite in the following way (Michaelis and Arend, *loc. cit.*, p. 266). Thirty grams of ammonium hypophosphite were dissolved in 100 grams of glacial acetic acid, and 45 grams of acetic anhydride were gradually added.

The mixture was warmed on the water-bath until a precipitate began to appear. It was then cooled, another 45 grams of acetic anhydride were added, and the mixture was heated again on the water-bath. Finally, the whole was poured into excess of water, filtered, washed, and dried. We experienced great difficulty in removing acetic acid from this precipitate by washing. The analysis shows that the substance cannot be the oxide, P_4O.

Sample V was prepared from sample IV by warming for some time on the water-bath with dilute hydrochloric acid. This removed the impurities to such an extent that the amount of phosphorus rose 1 per cent.

Sample VI was prepared from the red solution, obtained by dissolving sample IV in aqueous alcoholic potash, by precipitating with hot hydrochloric acid (one volume of strong hydrochloric acid to two volumes of water).

Analytical Results.—The analytical results obtained were:

Sample.	Percentage of *P*.	C.c. of hydrogen per 0·1 gram of substance.	Contraction		Residue per 0·1 gram. Gram.	Formula, assuming that the substance is a chemical compound, and neglecting residue.
			Found c.c.	Calculated for hydrogen, c.c.		
I.	86·7	11·14	17·06	16·71	0·0059	$P_4H_{1\cdot43}O_{1\cdot1}$
II.	92·87	8·87	13·35	13·31	0·0013 [1]	$P_4H_{1\cdot06}O_{0\cdot53}$
	92·81	8·13	12·17	12·19	0·0029	$P_4H_{0\cdot97}O_{0\cdot84}$
III.	90·01	7·05	contraction	not found	0·0052 [2]	$P_4H_{0\cdot87}O_{0\cdot78}$
		3·63 [3]	7·66	5·45 [4]		
IV.	86·50	7·55	12·97	11·33	0·0045 [5]	$P_4H_{0\cdot97}O_{1\cdot14}$
		4·72	7·43	7·07		
V.	87·58					
VI.	89·75	7·51				$P_4H_{0\cdot93}O_{0\cdot83}$

Since 0·1 gram was about the amount of substance taken, the hydrogen is calculated as c.c., and the residue as grams per 0·1 gram of substance.

In calculating the formula in the last column, no allowance is made for the residue, and therefore the number attached to the oxygen is somewhat too large.

The second value for the hydrogen with samples III and IV was obtained when the substance was distilled in a tube which contained no copper or aluminium. It was smaller because the water vapour was not decomposed.

[1] In this experiment, the residue was heated with a solution of potash, and then washed with water, proving that a considerable portion is insoluble in potash.

[2] This residue gave, on combustion with lead chromate, 0·0006 gram of carbon.

[3] This does not represent all the hydrogen which can be obtained by heating alone, since during the experiment the stopper came out of the little bottle, and some of the "suboxide" was blown through the tube by the escaping hydrogen.

[4] The absorption which occurred on the addition of potash after explosion was 0·77 c.c.

[5] The residue gave, on combustion with lead chromate, 0·0009 gram of carbon.

Michaelis and Pitsch's Pure and Impure Suboxides.

Michaelis and Pitsch distinguish between *impure* suboxides, which are supposed to contain red phosphorus and solid phosphoretted hydrogen, and *pure* suboxides, free from these substances. The following are their analytical numbers for the impure preparations:

P	90·35 ; 90·1	89·80 ; 89·72	90·48	90·89	91·85 per cent.
H	1·73	0·3	1·36	0·95	1·95 ,,

The calculated percentage of hydrogen in the compound P_4H_2 is 1·58, and therefore some of the impure suboxide specimens contain more hydrogen than the solid hydride of phosphorus to which the impurity is supposed to be due. Again, there is nothing in the methods of preparation of the impure and pure substances to suggest such a marked difference in composition as the authors claim for them. For example, a pure suboxide containing no hydrogen is obtained by the action of acetic anhydride on ammonium hypophosphite, and an impure substance, containing a large percentage of hydrogen, by the action of acetyl chloride on hypophosphorus acid.

Our analytical numbers afford a strong confirmation of the view already expressed that the "suboxide of phosphorus" is only impure red phosphorus.

The Red Solution of Phosphorus in Aqueous Alcoholic Potash.—When ordinary phosphorus is dissolved in aqueous alcoholic potash, a red solution is obtained. The solution, when first formed, is apparently quite clear, but on allowing it to remain at the temperature of the laboratory, it rapidly decomposes with evolution of hydrogen and phosphoretted hydrogen, and loss of colour. If a strong solution is allowed to decompose, it becomes muddy, and a brown solid slowly settles to the bottom. When the solution is kept at 0°, the same changes take place, but much more slowly. On warming on the water-bath, the decomposition proceeds very rapidly, and no brown solid is formed. The point to be borne in mind is that the red solution itself, when separated from the phosphorus from which it is obtained, is at the ordinary temperature very unstable, and readily decomposes with evolution of hydrogen and phosphoretted hydrogen. Now, some stress has been laid by Michaelis and Pitsch upon the supposed fact that ordinary phosphorus is soluble in aqueous alcoholic potash with evolution of hydrogen, whereas the "suboxide" dissolves in it without liberation of this gas, which would indicate, if the observation were correct, that phosphorus must be partially oxidised before solution can take place. On performing comparative experiments, we find that the "suboxide" and ordinary phosphorus dissolve in aqueous alcoholic

potash at the ordinary temperature, in both cases with evolution of considerable quantities of hydrogen. At 0°, the "suboxide" dissolves very much more rapidly than ordinary phosphorus, and in neither case is an appreciable quantity of hydrogen given off. The hydrogen can, therefore, in all cases be regarded as derived from the decomposition of the red solution, and certainly affords no evidence of the state of oxidation of the substances dissolved. No conclusions can be drawn from the relative rates of solution of the two substances, since the particles of the one are so small that their shape can scarcely be seen under a microscope (one-sixth inch objective), whereas the granules of the other can readily be seen with the naked eye. If ordinary phosphorus could be obtained as finely divided as the "suboxide," there is every reason for thinking that the red solution would be formed at least as readily in the one case as in the other.

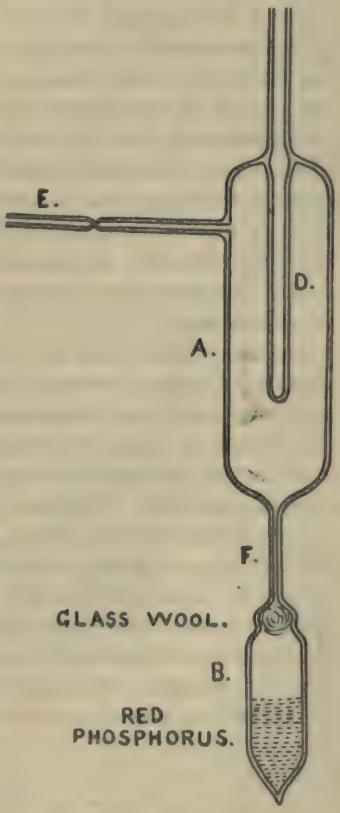
The red solution may be precipitated either by neutralisation with an acid, or by the addition of an ammonium salt. The colour of the precipitate obtained with a strong acid is light yellow or green, with a weak acid it is a darker green, and with ammonium chloride it is still darker. The dark precipitates, when warmed with a strong acid, become bright yellow, indicating that the dark colour is probably due to the presence of a base in the precipitate, which can only be completely removed by a strong acid. The substances obtained in the absence of any base are always bright yellow, such, for example, as the "suboxide" formed by the action of acetic anhydride on hypophosphorus acid. It may here be mentioned that the brown solid, obtained by the decomposition of the dark red solution, becomes bright yellow when warmed with hydrochloric acid.

Michaelis and Pitsch assert that certain specimens of *impure* "suboxide" leave a residue of red phosphorus when dissolved in aqueous alcoholic potash. All our preparations, whether they contain 94 per cent. or only 86 per cent. of phosphorus, are completely soluble in this reagent, and a precipitate is formed only on allowing the resulting clear red solution to stand.

Concerning the nature of the red solution, it may be pointed out that the presence of alcohol greatly accelerates the solution of flowers of sulphur in potash, persulphides being formed. By analogy, we are led to suspect that the solution of phosphorus in the same reagent contains a perphosphide. This supposition, if correct, would account for its colour, and for the precipitation of phosphorus on the addition of an acid. The potassium phosphide is soluble in alcohol with formation of a deep red solution, but the reaction is so violent that it is attended with considerable decomposition.

Solubility of Red Phosphorus in Aqueous Alcoholic Potash.

Besides establishing a very close relationship between the so-called suboxide of phosphorus and red phosphorus in other respects, Chapman and Lidbury have shown that Pedler's phosphorus (obtained by the action of sunlight on a solution of phosphorus in carbon disulphide) is, like the "suboxide," soluble in aqueous alcoholic potash. This form of phosphorus was used because it can easily be obtained in a fine state of division. Michaelis and Arend find that this phosphorus contains, as might be expected, both carbon and sulphur, and they believe that some oxygen is also present, which is derived from the wash-water by the substitution of oxygen for sulphur. By using carbon tetrachloride in the place of carbon disulphide as a solvent for the phosphorus, they obtained, by the action of sunlight, a substance which they were unable to dissolve in aqueous alcoholic potash. It is not, however, necessary to consider the experiments of Michaelis and Arend on this point in detail, since the complete solubility of red phosphorus in aqueous alcoholic potash is so easily proved that it cannot for a moment be doubted. To establish this fact, the following experiments were performed.



The apparatus employed to prepare the red phosphorus is shown in the accompanying diagram. The tube *B* was partially filled with red phosphorus, which was prevented from entering *A* by means of a tight plug of glass wool. The red phosphorus, before being introduced into the tube, was washed in turn with water, alcohol, and ether, and dried in a vacuum over phosphoric oxide. The T-piece, *E*, was fused on to a tube, which communicated through a phosphoric oxide tube with an automatic Sprengel pump in such a manner that *A* and *B* were horizontal. After exhaustion, the phosphorus was very slowly distilled into *A*. During the distillation, a little hydrogen was evolved which was pumped out of the apparatus after sufficient phosphorus

had come over. The tube *A* was finally fused off at *E* and *F*, and the phosphorus was distilled into the end remote from the tube *D*. The ordinary phosphorus may be *completely* reconverted into red phosphorus by passing the silent discharge through the vapour. This was done by connecting one pole of an induction coil with copper wire wrapped round the middle of the tube *A*, and the other pole with mercury contained in *D*. The conversion takes place only slowly at the ordinary temperature on account of the low pressure of the vapour; it is, however, accelerated by heating the tube to 100° in an air-bath. The red phosphorus was deposited over the inner surface of the tube. When it was thought that the conversion was complete, the tube was opened under carbon disulphide, and allowed to remain in contact with this liquid for some hours. The carbon disulphide did not leave any residue of phosphorus on evaporation. The red phosphorus was finally removed from the walls of the tube, ground in a mortar, collected on a filter paper, and washed with ether. On treating the product with aqueous alcoholic potash, a deep red solution passed through the filter paper, and this gave a voluminous precipitate with hydrochloric acid. A residue consisting of much larger grains distinctly visible to the naked eye remained behind, which was rendered soluble by regrinding.

The same experiment may be performed with commercial red phosphorus. The sample used by us was in the form of a powder, and did not contain ordinary phosphorus. It was reduced to a fine powder by grinding in an ordinary porcelain mortar. An agate mortar cannot be used for this purpose as its surface is so smooth that the pestle slides over the particles. The fine powder, after being washed successively with hydrochloric acid, alcohol, and ether, was readily soluble in aqueous alcoholic potash, giving a considerable quantity of a deep red solution, which was then precipitated by hydrochloric acid. The residue remaining on the filter paper was easily rendered soluble by regrinding. By repeating the process of grinding several times, all the phosphorus, with the exception of a small quantity which could not be removed from the filter paper, was converted into the red solution.

Conclusions.

From the experiments described in this paper, and from the facts established by Chapman and Lidbury, we conclude:

(1) That no suboxide of phosphorus having the formula P_4O has ever been prepared, because the percentage of phosphorus is variable, and because the latest substance, described as having the composition P_4O, contains other elements in addition to phosphorus and oxygen, hydrogen being present in considerable quantity.

(2) That the substance described as a suboxide of phosphorus is impure red phosphorus, because the properties of both are the same, and because direct analyses have shown that the impurities in the alleged suboxide (regarding it as red phosphorus) are such as might be expected from the methods of preparation.

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CXXXII.—*The Action of Ammonia on Metals at High Temperatures.*

By George Thomas Beilby and George Gerald Henderson.

Ten years ago, while one of the authors was engaged in developing an industrial process which involved the passing of large volumes of ammonia gas through metal tubes at a red heat, some striking observations were made. In the first place, the statement of Ramsay and Young (Trans., 1884, **45**, 88) that ammonia is decomposed into its elements with great rapidity by red hot iron was amply confirmed. When a current of ammonia at the rate of 4 litres per minute was passed through an iron tube 12·5 mm. in diameter and heated at 810° for 300 mm. of its length, only 27 per cent. of the ammonia escaped decomposition, 73 per cent., or nearly three-fourths of the whole, being decomposed. The velocity of the current through the heated part of the tube was about 1·5 metres per second, so that the ammonia molecules were only exposed to the hot metal for one-fifth of a second. Various observers had found that, for equal surfaces, copper has much less action on ammonia than iron. Experiments were accordingly made, using a solid drawn copper tube instead of an iron one. Under similar conditions of temperature and ammonia current, the quantity of ammonia decomposed by the copper tube in a given time was only about one-third of the quantity decomposed by the iron tube. This result was, so far, encouraging, and an attempt was made to use copper tubes for the industrial operation. However, after exposure to ammonia at a temperature of 800° for a few hours, the tube became so short and brittle that it could not bear its own weight without breaking. The next step taken was to strengthen the copper tube by slipping over it a sleeve pipe of iron, which fitted tightly and gave the necessary strength to resist bending or breaking. Thus protected, the copper tube could not break or crumble away, but it was soon found that it tended to close up until only a very small amount of gas could pass through it. Examination showed that the walls of the copper

tube had become very much thickened, and being unable to expand outwards, owing to the sleeve of iron, had expanded inwards until the bore of the tube was nearly closed. Observation with the microscope showed that the copper had become spongy and disintegrated throughout. It retained its colour, and, to a certain extent, its metallic lustre, but it appeared as if it had been in the fluid state, and blown up into a sponge by innumerable minute gas bubbles. Not only was the copper acted on, but the iron sleeve pipe had been reached and penetrated by the ammonia molecules. The iron pipe had become as brittle as hardened steel, so that it could be shattered by a blow with a hammer, and showed a bright, silvery fracture. Under the microscope, the iron also exhibited a spongy structure.

At this time, a number of other metals and alloys were experimented with, in the hope that something might be found which would resist the action of ammonia at a high temperature. Nickel, silver, platinum, gold, as well as a variety of alloys, were tried, but in every case the metal acquired the same spongy structure, and its strength and tenacity became seriously deteriorated. No metal we have tried is able to resist the attack of the ammonia molecule at a high temperature. To the already long list of the formidable properties of the nitrogen atom must now be added this power of attacking and disintegrating the most massive and refractory of metals, not even the noble metals being proof against its assaults.

In the case both of the iron and the copper tubes, it was found that under uniform conditions the quantity of ammonia decomposed remained fairly constant. While the continued action of ammonia tends to disintegrate the copper more and more, the greater surface thus exposed does not appear to add sensibly to the decomposition of ammonia by a given mass of metal. During the whole life of the protected copper tube (about 150 hours), the amount of ammonia decomposed did not vary much from 1 gram per minute. On the total life of 150 hours, this amounted to 9000 grams. This quantity of ammonia was many times the weight of the copper which decomposed it. It was evident, therefore, that the amount of ammonia decomposed was not in any way limited to what would be required to form a nitride or a hydride of copper. Examination of the decomposed gases showed that, on the average, the nitrogen and hydrogen were present in the proportion of 1 : 3 by volume. On the other hand, the appearance of the metals after exposure to ammonia clearly indicated that the melting point of the metal had been lowered by the action, and, therefore, that chemical combination between the metal and one or other of the gases had taken place at some stage in the operation. To produce a spongy mass, the metal must have been, at any rate, in a plastic or semi-fluid condition, but the structure rather suggested that

the metal had been suddenly cooled while in the act of boiling, bubbles in every stage of formation and bursting being fixed in the solidified metal. A spongy state may be produced in a material which is merely plastic, but this appearance of boiling could only be found in a material which had been fairly fluid. The temperature of the experiment was far below the melting point of copper or iron, therefore at some stage in the operation a more fusible compound must have existed. As everything pointed to the continuous formation and decomposition of some compound of the metal with ammonia or one of its constituent elements, some preliminary experiments were made to ascertain how far combination was taking place. Rolls of fine wire gauze of copper and of iron were heated in a porcelain tube at 800°, and a current of ammonia at the rate of 6·5—7 litres per minute was passed through the tube for 70 minutes. The following results were obtained. Weight of copper gauze before treatment, 42·04 grams; after treatment, 43·92 grams—a gain of 1·82 grams, or 4·47 per cent. Weight of iron gauze before treatment, 18·87 grams; after treatment, 20·02 grams—a gain of 1·15 grams, or 6·09 per cent. The iron gauze had become so brittle that it could not be bent without breaking. Its colour was bright silvery-grey, and under the microscope the spongy structure was very well marked. The copper gauze had become equally brittle. Its colour was a bright pink, and its surface was so completely disintegrated that metallic lustre had disappeared. Under the microscope, the bubble structure was very obvious. With both metals, the diameter of the wires had increased two or three times.

As already stated, a number of other metals were exposed to ammonia at a red heat. Although the energy of the action varied to some extent, all without exception were attacked in the same way, and became spongy and disintegrated. Even in the case of those metals, for example, gold and platinum, which did not show any obvious increase in weight through absorption of nitrogen, the appearance under the microscope was the same, and indicated that the action of ammonia had produced a certain degree of fluidity. This was shown in an interesting way when wires of different metals were twisted together and then heated in a current of ammonia. In many cases it was found that these metals had flowed together; thus, iron and copper, iron and gold, gold and platinum, gold and silver, became fused together. In the case of iron and gold, the gold sometimes flowed over the surface of the iron, forming a complete plating.

Up to this point, the investigation of this matter had been prosecuted mainly with the object of finding a suitable material for making tubes to resist the action of ammonia at a red heat. Two years ago, the authors began a more systematic examination of the behaviour of various metals under the action of ammonia. The scope of the inves-

tigation was not restricted to the study of the chemistry of certain nitrides, but was intended to cover the physical as well as the chemical action of gases on metals at high temperatures. The remarkably energetic action of ammonia on all metals at a high temperature, and the interesting physical changes in the metals brought about by this action, very naturally suggest that this particular case of the mutual action of gases and metals may supply a key to the study of the whole subject. It is not possible to examine the specimens of various metals which have been subjected to this action without being impressed with this view of the phenomenon and its probable bearing on the whole question of the occlusion of gases by metals, and the permeability of metals by gases.

The general method of experiment followed has been to pass a current of dry ammonia gas over the metals in the form of rod, wire, sheet, or foil, or sometimes in a fine state of division. The metals were placed in a porcelain tube, glazed inside and outside, and heated in a gas furnace to varying degrees of redness. The temperature was determined sometimes by the melting of pure salts and sometimes by a Le Chatelier thermo-junction. In the experiments carried out at temperatures below 500°, the tubes containing the metal were heated in a Meyer air-oven. As a general rule, a very rapid current of ammonia was passed through the tube, since experience showed that it was desirable that the gas should be present in large excess. After each experiment, the specimen of metal was left to cool in a current of ammonia before removal from the tube. Preliminary experiments proved that little or no decomposition of the ammonia resulted from passing the gas through a glazed porcelain tube 50 cm. in length and 12·5 mm. in internal diameter, even at a temperature of 850°. Many series of experiments were carried out in which the conditions were varied with respect to the state of aggregation of the metal, the velocity of the current of ammonia, the temperature to which the metal was heated, and the duration of the experiment. The results of the numerous experiments are summarised in the following paragraphs.

Iron.

In January last, Mr. G. J. Fowler published an exhaustive paper on the formation of iron nitride by the action of ammonia on finely divided, freshly reduced iron (this vol., p. 285). Our independent conclusions as to the formation and decomposition of iron or copper nitride (arrived at nearly ten years ago as a result of working on an industrial scale), namely, that formation of the nitride occurs in presence of excess of ammonia molecules, whilst decomposition takes place when hydrogen molecules are present in excess, are completely confirmed by

Fowler's experiments with iron. We do not, therefore, propose to publish results which are simply a repetition of his, but as the conditions under which many of our experiments were carried on were different, we give a summary of our conclusions.

In the experiments upon iron, the metal was used in the form of fine gauze, wires of different thickness, or rods. The general results of a large number of trials under varying conditions were as follows.

When iron in the compact state is heated in a current of ammonia under the necessary conditions, it is more or less completely converted into a nitride of iron of the formula Fe_4N_2,* which possesses characteristic properties of its own. A nitride of this formula contains 11·13 per cent. of nitrogen. We obtained products containing up to 10·59 per cent. of nitrogen, although, if the conditions were not favourable, smaller proportions of the nitride were formed.

The essential conditions for the formation of nitride of iron by the direct action of ammonia on iron in the compact state are, first, the presence of ammonia in large excess, and second, a sufficiently high temperature. If these conditions are satisfied, the action takes place with remarkable rapidity. An iron rod one-quarter of an inch in diameter was penetrated to the centre in 30 minutes when heated to bright redness in a rapid current of ammonia.

Unless care is taken to ensure the presence of a large excess of ammonia, very little or absolutely none of the nitride is obtained, but at the same time, the ammonia is more or less completely decomposed into its elements and the physical properties of the iron undergo an extraordinary change. It becomes highly lustrous and very brittle, and when examined under the microscope exhibits no trace of crystalline structure, but only the porous or spongy structure already referred to. It is evident that, under the conditions of our experiments, nitride of iron is not stable except in presence of excess of ammonia, and that the great alteration in the structure of the iron, even when no nitrogen is permanently fixed, is due to the continuous formation and decomposition of the nitride.

Nitride of iron can be produced from the compact metal within a fairly wide range of temperature. According to our experiments, the formation of the nitride begins somewhat below 450°, although the action is very slow at that temperature, and the nitride can also be produced at the highest temperature attainable in our furnace (850—900°). There is, however, no reason to suppose that the latter temperature represents the highest limit at which the formation of nitride is possible. The most favourable temperature depends largely upon the state of aggregation of the iron, and particularly upon the

* The formation of this nitride was first established by Stahlschmidt (*Ann. Phys. Chem.*, 1864, [ii], **125**, 37).

surface exposed to the action of the ammonia. Thus, using a fine wire of 0·3 mm. diameter, the action proceeded most rapidly, and the largest proportion of nitride was obtained at a temperature somewhat below 650°, but when thicker wires or rods were used the most suitable temperature was found to be 800—850°.

As regards the properties of nitride of iron, our results generally corroborate those of Fowler. The nitride is very readily soluble in dilute hydrochloric or sulphuric acids, and it was proved by analysis that the whole of the nitrogen is then liberated in the form of ammonia. When heated to redness in a current of hydrogen, it is completely decomposed into iron and ammonia, and it is also decomposed when exposed to the action of steam at a red heat. It can, however, be heated to a high temperature in a current of ammonia without undergoing any change. Iron gauze or wire, when converted into nitride, acquires a silvery-grey colour and retains its external form, but the surface is penetrated by innumerable cracks and acquires a peculiar, "blistered" appearance, whilst in the case of the thicker wires the surface is also dotted over with crater-like openings with raised edges, as if bubbles of gas had forced their way through a fused or semi-fused mass. The product is so brittle that it can easily be broken into fragments with the fingers, and crushed to powder in a mortar. Under the microscope, the powder appears to consist of aggregates of lustrous, silvery particles, more or less spherical in form, which evidently had solidified from a fused, or at least pasty, state. When experiments with thick wires or rods were interrupted after passing the ammonia for short periods, a core of unaltered iron remained, whilst the outermost part was wholly converted into nitride.

Pure iron is rendered hard and brittle like steel by the absorption of small quantities of nitrogen. Tubes of malleable iron, after exposure for 7 days to the action of ammonia at 800°, became so brittle that they could be broken like porcelain by a blow with a hammer, and a rod of charcoal iron was made so hard that it could be used as a drill. It appears not improbable, in the authors' opinion, that some at least of the effects on the structure and properties of iron and steel which are at present attributed to other elements may in reality be due to the presence of traces of nitrogen.

The conflicting statements of earlier observers regarding the action of ammonia on iron at high temperatures can be reconciled if it is remembered, first, that although the physical properties of the metal are altered, no nitride is permanently formed unless the necessary conditions are observed; and second, that the proportion of the metal converted into nitride in a given time is dependent on the state of aggregation of the iron, as well as on the temperature and the quantity of ammonia present.

Cobalt.

In preparing cobalt nitride, we used the metal in the form of the powder obtained by reducing pure oxide of cobalt with hydrogen. When heated at a high temperature in ammonia, cobalt behaved similarly to iron as regards the decomposition of the ammonia into its elements, but no nitride was formed. At a temperature of about 500°, a slight increase in the weight of the metal was noted, and at a somewhat lower temperature the metal combined slowly with nitrogen until finally a product containing 10·33 per cent. of nitrogen was obtained. A nitride of cobalt of the formula Co_4N_2 contains 10·63 per cent. of nitrogen, hence the conversion of the cobalt into nitride was practically complete. The formation of nitride of cobalt can only proceed within much narrower limits of temperature than that of nitride of iron, even when, as in all our experiments, ammonia is present in large excess. Thus, for example, a sample of cobalt which gained in weight slowly when heated in ammonia at 500°, lost again when the temperature was raised to 600°. The most favourable temperature for starting the formation of the nitride appears to be about 470°; once the absorption of nitrogen has begun, the temperature may with advantage be lowered somewhat below this point.

Nitride of cobalt was obtained as a dull greyish-black powder. Under the microscope, the particles of powder are seen to be composed of aggregations of minute particles which are all more or less lustrous and to some extent spherical in form, as if they had been at any rate in a semi-fluid condition. The nitride dissolves rapidly and completely in dilute hydrochloric and sulphuric acids with formation of a cobaltous salt, and analysis showed that all the nitrogen is set free as ammonia. It is completely decomposed when heated to redness in hydrogen, the nitrogen being eliminated as ammonia, and it is also decomposed, slowly but completely, when heated in a current of steam.

Nickel.

In some of our experiments, the nickel was used in the form of wire 2 mm. in diameter. When the wire was heated in ammonia at a high temperature (800—850°), no increase in weight was noted, but the ammonia was, to a large extent, decomposed into its elements, and the appearance of the metal was greatly altered. The surface became quite dull at first, and was soon penetrated by an irregular network of cracks, and the metal became quite brittle. When the temperature was lowered to about 600°, the metal began to gain in weight slowly, and after several hours' heating in a rapid current of ammonia, an increase of 5 per cent. in weight was attained. By dissolving some of the

product in dilute sulphuric acid, and estimating the ammonia liberated, it was proved that this increase was due to the formation of nitride of nickel. After this treatment, the surface of the wire was found to be penetrated by cracks and fissures, spreading in all directions, and the metallic lustre had quite disappeared. Under the microscope, the product was seen to be composed of minute, closely adhering particles, which were silvery in appearance, and all more or less spherical in form. Nitride of nickel, apparently, cannot be obtained at temperatures much above 600°; at about 550°, it is produced fairly rapidly, but it is of advantage to lower the temperature somewhat once the process has started. Little or no nitride is obtained below 400°.

As in the case of iron, the essential conditions for the formation of nitride of nickel are the presence of ammonia in excess and a suitable temperature; under other conditions, no nitrogen is permanently fixed by the metal, but the ammonia is largely decomposed, and the properties of the metal are profoundly modified, owing to the continuous formation and decomposition of the nitride. The range of temperature within which nitride of nickel can be formed appears to be much narrower than in the case of iron, but, on the whole, there is great similarity in the behaviour of the two metals when exposed to the action of ammonia at high temperatures.

In order to prepare nickel nitride, finely divided nickel, obtained by reduction of the oxide with hydrogen, was heated in ammonia at about 500°. The metal gained in weight steadily but slowly until a product was obtained which, on analysis, was found to contain 7·5 per cent. of nitrogen. In none of our experiments was the metal induced to combine with a higher proportion of nitrogen than this. The formula Ni_3N requires 7·36 per cent., and the formula Ni_5N_2, 8·74 per cent. of nitrogen, and hence it appears that the nitride of nickel obtained in our experiments differs in composition from the nitrides of cobalt and iron. It was produced as a dull black powder, which was shown by the microscope to consist of aggregates of very minute, roughly spherical particles adhering closely together. It is readily soluble in dilute hydrochloric and sulphuric acids, and resembles the nitrides of cobalt and iron in its behaviour when heated in hydrogen and in steam.

Copper.

Copper, like iron, is very sensitive to the action of ammonia at high temperatures, and there is considerable similarity in the behaviour of the two metals.* If the ammonia is in large excess, the copper is converted, at least partially, into a nitride, which, however, is only stable

* The statements of earlier observers regarding the action of ammonia on copper at high temperatures are very contradictory.

under definite conditions, and is readily decomposed into its elements. Hence no nitride is formed when copper is heated in ammonia unless a large excess of the latter is present, but on the other hand, the ammonia is decomposed into hydrogen and nitrogen (although the amount of the decomposition is only about one-third of that effected by iron under similar conditions), and the metal suffers a very marked change in its physical properties. It loses most of its metallic lustre, acquires a pink colour, develops much the same spongy structure as has been described in the case of iron, and becomes extremely brittle. Examination with the microscope leads to the conclusion that the metal has been in at least a semi-fluid state, and has been rendered porous and spongy by the escape of numerous minute bubbles of gas. The ammonia penetrates into the metal very quickly. For example, a copper rod, one-quarter of an inch in diameter, was attacked through to the centre when heated in a current of ammonia for 30 minutes. But disintegration of the metal goes on almost indefinitely. Copper exposed to the action of ammonia for seven days at 800° became reduced to a fine, spongy powder.

In our experiments, the metal was used in the form of gauze, wire, foil, and rod. The maximum quantity of nitrogen fixed in any experiment was 4·5 per cent. A nitride of copper of the formula Cu_3N contains 6·86 per cent. of nitrogen. The nitride is very easily decomposed by heating in hydrogen, and apparently can only exist within a comparatively narrow range of temperature. The change in the physical properties of the metal, even when no nitrogen is retained by it, is no doubt to be attributed in this case also to formation and decomposition of the nitride.

Silver, Gold, and Platinum.

In our experiments with silver, gold, and platinum, the metals were used both in the form of wire and in the spongy state. They were heated in ammonia at temperatures varying from 400° up to nearly 900°, but in no case was the formation of a nitride indicated by any increase in the weight of the metal, however rapid the stream of ammonia through the tube. In every instance, however, the ammonia suffered decomposition into its elements, although to a far smaller extent than with the metals of the iron group, and the physical properties of the metals were altered, to some extent in all cases, and very markedly in the experiments conducted at temperatures from 750° upwards.*

* "Ammoniacal gas is scarcely acted on in an ignited porcelain tube when clean and empty, but more readily when it contains fragments of porcelain; with still greater facility when it contains platinum, silver, or gold wire; more easily still when it contains copper wire, and most quickly and completely when iron wire is

When heated in ammonia at 800°, the polished surface of fine silver wire acquired a "frosted" appearance, and when examined with the microscope the wire was found to be covered all over with minute rounded blisters or bubbles, while there was also very distinct evidence of "spitting." The elasticity of the metal was also very greatly reduced.

Gold wire was also greatly changed in appearance by exposure to the action of ammonia at 800°. The colour was changed, and the entire surface of the wire was seen under the microscope to be closely covered with small blisters or protuberances which appeared to have solidified after partial fusion. When precipitated gold was similarly heated in ammonia, the brown masses shrank together and became much more compact, the colour changed to light yellow, and metallic lustre made its appearance. The microscope showed that the product was composed of roughly spherical particles which adhered closely. When a current of ammonia was passed at the rate of 2 litres per hour over gold heated at 800°, fully 10 per cent. of the gas was decomposed.

When platinum wire was heated in ammonia at 800°, the surface of the metal became duller, less lustrous, and showed a more or less blistered appearance under the microscope. In most cases, a fine, black deposit was formed on the surface of the metal. The deposit was sometimes closely, sometimes loosely, adherent, but could be rubbed off easily with filter paper or cotton wool. On examination, it was found to be nothing but platinum black, which clearly had been formed by disintegration of the surface of the compact metal. When a rapid current of ammonia was passed over platinum wire heated at 800°, the gas was decomposed to the extent of about 8 per cent.

The elasticity of both gold and platinum, like that of silver, is reduced to an enormous extent by exposure to a current of ammonia at high temperatures, and the resistance of each metal to the passage of an electric current is perceptibly increased.

Comparison of our experiments on silver, gold, and platinum with those on the metals of the iron group and on copper, leads to the conclusion that the very marked change in the physical character of the former metals, which is produced by the action of ammonia on them at high temperatures, is likewise due to the formation of metallic nitrides, which, however, are quite unstable, even in presence of a great excess of ammonia, and therefore readily decompose into metal and nitrogen. The continuous formation and decomposition of these nitrides would, of course, account for the observed disintegration of

introduced. These metals, for the most part, do not undergo any observable alteration in weight; but copper and iron become brittle, while gold and platinum remain perfectly unchanged."—GMELIN, *Handbook of Chemistry*, vol. II., p. 421.

the metals under the attack of strongly heated ammonia. The instability of these nitrides probably arises from their temperatures of formation and decomposition lying close together. It seems not improbable that the formation of spongy deposits on the outside of platinum crucibles heated by Bunsen burners, as well as the disintegration of the platinum wires of pyrometers exposed to furnace gases, may, sometimes at least, be accounted for by the presence of traces of ammonia in the furnace gases.

Conclusions.

A number of other metals, including aluminium, zinc, tin, and lead, and many different alloys, for example, brass and aluminium bronze, have also been examined with regard to their behaviour when subjected to the action of ammonia at temperatures below their melting points. In every case, changes in the physical structure of the metals and alloys similar to those already described have been observed, and the ammonia has been decomposed to a varying extent into nitrogen and hydrogen. It would be tedious and unprofitable to describe our experiments in detail; suffice it to say that they all tend to confirm the following general conclusions at which we have arrived.

Metals in general, when exposed to the action of ammonia at high temperatures, are either converted into nitrides—wholly or partially—or else profoundly changed in their physical properties, even although no nitrogen is permanently fixed by the metal. The changes include alterations in the colour, lustre, tenacity, elasticity, and electrical conductivity of the metals, and are caused by the disintegration of the metal due to the continuous formation and decomposition of unstable nitrides. When the altered metals are examined under the microscope, it is seen that these nitrides must be more fusible than the metals, for a characteristic spongy structure, due to the escape of innumerable minute bubbles of gas from a molten or pasty mass, is clearly visible in all cases. The maximum absorption of nitrogen by each metal is determined by (1) the state of aggregation of the metal, (2) the temperature, (3) the excess of ammonia, (4) the time. Nitrides can hardly be obtained by the direct action of ammonia on metals at high temperatures unless an excess of ammonia is present, since all are easily decomposed into metal and nitrogen by heating in hydrogen.

If we follow the action closely, for example, in the case of copper, it appears probable that it begins by the ammonia molecules attacking the surface molecules of the metal and forming a fusible nitride. If a plentiful excess of ammonia molecules are present to overpower the hydrogen molecules which result from the decomposition of the ammonia, a theoretical absorption of nitrogen takes place. But the

nitride which is formed, being fusible at the temperature of formation, penetrates into the copper, and the further action tends to take place at some distance from the surface, where the ammonia molecules are fewer, and the hydrogen molecules are relatively more numerous. At a certain distance from the surface, a point will be reached at which the ammonia and the hydrogen molecules so exactly balance each other that no nitrogen is absorbed, or rather that, as soon as a molecule of nitride is formed, it will be immediately decomposed with evolution of nitrogen. The hydrogen resulting from the decomposition of the ammonia, together with the nitrogen from the decomposition of the nitride, force their way to the surface of the fluid nitride, causing the appearance of boiling—the particular structure which is found in all metals which have been acted on by ammonia.

It is clear that some such explanation as this is necessary if we are to account for the continuous and practically constant decomposition which takes place at a given metallic surface, and for the disintegration of the metal itself. We hope to extend our investigations on the action of gases on metals in the near future.

We take this opportunity of expressing our thanks to Messrs. P. W. Tainsh, A.I.C., and F. W. Watson, B.Sc., Nobel Company's Prizemen, and B. G. McLellan, A.I.C., Research Student in the Glasgow and West of Scotland Technical College, for much assistance in the experimental part of this investigation. We are also greatly indebted to Messrs. Johnson and Matthey, London, for their courtesy in preparing and placing at our disposal the pure gold and platinum which we required.

GLASGOW.

CXXXIII.—*Condensation of Benzil with Dibenzyl Ketone.*

By GEORGE GERALD HENDERSON and ROBERT HENRY CORSTORPHINE, B.Sc.

IN the course of his researches on the synthesis of pentacarbon rings, Japp has shown that benzil and acetone unite, in presence of a small quantity of aqueous caustic potash, to form the aldol condensation product acetonebenzil, $COPh{\cdot}CPh(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3$, and that when acetonebenzil is treated with an excess of the same reagent, it is converted, by elimination of the elements of water, into anhydracetonebenzil (Japp and Miller, Trans., 1885, 47, 21; Japp and Burton, Trans., 1887, 51, 420; Japp and Lander, Trans., 1897, 71, 123). Japp ultimately came to the conclusion that anhydracetonebenzil is a closed

chain compound, namely, a diphenyl*cyclo*pentenolone of the formula $\begin{matrix}\mathrm{CPh}=\!=\!=\mathrm{CH}\\ |\\ \mathrm{CPh(OH)\cdot CH_2}\end{matrix}\!\!>\mathrm{CO}$, and on substituting dibenzyl ketone for acetone, we obtained results which support this view.

Benzil condenses readily with dibenzyl ketone in presence of aqueous caustic potash, yielding a substance of the formula $C_{29}H_{22}O_2$, which, from its general character, appears to be a *tetraphenyl*cyclo*pentenolone*, a derivative of 1 : 2 : 4 : 5-tetraphenyl*cyclo*pentene. The reaction may be represented by the equation :

$$\begin{matrix}\mathrm{COPh}\\ |\\ \mathrm{COPh}\end{matrix}\!\!>\mathrm{CO} + \begin{matrix}\mathrm{CH_2Ph}\\ |\\ \mathrm{CH_2Ph}\end{matrix}\!\!>\mathrm{CO} = \begin{matrix}\mathrm{CPh}=\!=\!=\mathrm{CPh}\\ |\\ \mathrm{CPh(OH)\cdot CHPh}\end{matrix}\!\!>\mathrm{CO} + \mathrm{H_2O}.$$

An aldol condensation product is doubtless formed in the first instance, but we did not succeed in isolating it, although the conditions of the reaction were variously modified with that object in view. The general behaviour of the new compound is in accordance with the formula given above, the chief point of difference being that the compound does not combine additively with bromine to form a dibromide, as might be expected from its constitution, but yields a very unstable substitution derivative. On the other hand, it responds to Baeyer's test for non-saturation, as it rapidly changes the colour of a solution of potassium permanganate in the cold in presence of excess of sodium carbonate. The existence of a hydroxyl group in the compound is proved by the formation of an *acetyl* derivative, as also by the action of phosphorus pentachloride and of alcoholic hydrogen chloride on it, when an unstable chlorine derivative of tetraphenyl-*cyclo*pentenone is obtained in each case by replacement of the hydroxyl group. The compound yields a crystalline *oxime*, and, although it does not react readily with phenylhydrazine itself, a *hydrazone* was prepared by heating it in alcoholic solution with *p*-bromophenylhydrazine. When cautiously oxidised with chromium trioxide in acetic acid solution, it yields benzoic acid and a neutral crystalline *compound*, $C_{28}H_{20}O_4$, which possibly may be *iso*benzil, $\begin{matrix}\mathrm{CPh\cdot O\cdot COPh}\\ ||\\ \mathrm{CPh\cdot O\cdot COPh}\end{matrix}$.

By partial reduction of diphenyl*cyclo*pentenolone with hydriodic acid, diphenyl*cyclo*pentenone, $\begin{matrix}\mathrm{CPh\cdot CH_2}\\ ||\\ \mathrm{CPh\cdot CH_2}\end{matrix}\!\!>\mathrm{CO}$, is obtained (Japp and Burton, *loc. cit.*), but tetraphenyl*cyclo*pentenolone behaves somewhat differently with reducing agents, and does not give the expected tetraphenyl*cyclo*pentenone, $\begin{matrix}\mathrm{CPh}=\!=\!=\mathrm{CPh}\\ |\\ \mathrm{CHPh\cdot CHPh}\end{matrix}\!\!>\mathrm{CO}$. When it is heated under atmospheric pressure with hydriodic acid and red phosphorus, it gives a crystalline compound of the formula $C_{29}H_{24}O$, which apparently does not contain a carbonyl group, as it could not be induced to

form either an oxime or a hydrazone. On the other hand, the compound yields an *acetyl* derivative, and it also reacts readily with phosphorus pentachloride and with alcoholic hydrogen chloride, giving in each case the same *chlorotetraphenyl*cyclo*pentene*, $C_{29}H_{23}Cl$; the presence of a hydroxyl group in the compound is thus proved. With bromine, it gives, not an additive product, but a bromine derivative, $C_{29}H_{22}Br{\cdot}OH$; on the other hand, it quickly reduces potassium permanganate in presence of sodium carbonate, and hence appears to be unsaturated. We therefore conclude that this reduction product must be a *tetraphenyl*cyclo*pentenol*, of which the formula must be either $\begin{matrix}CPh{=\!=\!=}CPh\\ |\qquad\quad \diagdown\\ CPh(OH){\cdot}CHPh\end{matrix}\!\!>CH_2$, or more probably, $\begin{matrix}CPh{=\!=}CPh\\ |\qquad \diagdown\\ CHPh{\cdot}CHPh\end{matrix}\!\!>CH{\cdot}OH$.

When tetraphenyl*cyclo*pentenol is heated, under pressure, with hydriodic acid and red phosphorus at 170—180°, it undergoes further reduction, and a mixture of two hydrocarbons is obtained. One of these has the formula $C_{29}H_{24}$, and is in all probability 1 : 2 : 4 : 5-*tetra*-*phenyl*cyclo*pentene*, $\begin{matrix}CPh{=\!=}CPh\\ |\qquad \diagdown\\ CHPh{\cdot}CHPh\end{matrix}\!\!>CH_2$. The other hydrocarbon is apparently identical with the 1 : 2 : 4 : 5-tetraphenyl*cyclo*pentane, $\begin{matrix}CHPh{\cdot}CHPh\\ |\qquad\quad \diagdown\\ CHPh{\cdot}CHPh\end{matrix}\!\!>CH_2$, obtained by Wislicenus and Carpenter by the reduction of the pinacone, $\begin{matrix}CPh(OH){\cdot}CHPh\\ |\qquad\quad\quad \diagdown\\ CPh(OH){\cdot}CHPh\end{matrix}\!\!>CH_2$, which they prepared from dibenzoyldiphenylpropane (*Annalen*, 1898, 208, 223). The formation of the latter hydrocarbon justifies the view that the substance obtained by condensing benzil with dibenzyl ketone is a closed chain compound containing a pentacarbon ring.

Experimental.

*Tetraphenyl*cyclo*pentenolone*.

A mixture of 50 grams of benzil, 50 grams of dibenzyl ketone, and 100 c.c. of 33 per cent. aqueous caustic potash was heated gently on a water-bath, the contents of the flask being frequently mixed by vigorous shaking. After about half an hour's heating, the melted layer which floated upon the top of the aqueous solution began to solidify; when the whole had turned solid, the alkaline liquid was poured off, and the mass ground up in a mortar and then washed with water until quite free from caustic potash. The crude product was dark in colour, and even after repeated crystallisation from alcohol the crystals still retained a purple coloration. Part of the colouring matter was removed by washing the product with a little benzene, and the last trace got rid of by several crystallisations from benzene and

finally from alcohol. The yield was very satisfactory. The following results were obtained on analysis of the purified crystals:

0·2166 gave 0·6854 CO_2 and 0·1128 H_2O. C = 86·19; H = 5·78.
$C_{29}H_{22}O_2$ requires C = 86·56; H = 5·47 per cent.

A cryoscopic determination of the molecular weight, benzene being used as solvent, gave a result in accordance with the foregoing formula.

Wt. of substance.	Wt. of solvent.	Depression.	Mol. wt.	$C_{29}H_{22}O_2$ mol. wt.
0·1822	18·875	0·12°	394	402

Tetraphenyl*cyclo*pentenolone crystallises from alcohol in clusters of long, colourless, lustrous prisms which melt at 208°. It is readily soluble in benzene, and fairly readily in boiling alcohol, but only sparingly so in ether, and is almost insoluble in light petroleum. It dissolves in cold concentrated sulphuric acid, giving a solution of a beautiful, intense violet colour which quickly changes to red; from this solution, even after heating, it is precipitated by water unchanged, except that it is now coloured purplish-red. When a drop of a solution of potassium permanganate is added to an alcoholic solution of tetraphenyl*cyclo*pentenolone previously mixed with a few drops of aqueous sodium carbonate, the colour of the permanganate is very quickly discharged.

The *oxime*, $C_{29}H_{22}O{:}N{\cdot}OH$, was prepared by gently heating tetraphenyl*cyclo*pentenolone in alcoholic solution with the calculated quantities of hydroxylamine hydrochloride and sodium acetate, evaporating to dryness, extracting with ether, evaporating the ether, and recrystallising the product from alcohol. It crystallises in small, colourless plates which melt at 167° and are fairly easily soluble in alcohol. The following result was obtained on analysis:

0·2863 gave 8·6 c.c. moist nitrogen at 21° and 766 mm. N = 3·53.
$C_{29}H_{23}O_2N$ requires N = 3·35 per cent.

Tetraphenyl*cyclo*pentenolone does not react readily with phenylhydrazine. When an alcoholic solution of the two substances was heated for some time under a reflux condenser, no change took place; when the solution was heated in a sealed tube at 150°, a tarry mass was produced; and when a methyl alcoholic solution was heated at 100° for several hours in a pressure bottle, a small quantity of a yellow, crystalline substance was obtained which contained no nitrogen and was not further examined. However, by substituting *p*-bromophenylhydrazine for phenylhydrazine, the desired result was obtained. A solution in methyl alcohol of the calculated quantities of tetraphenyl*cyclo*pentenolone and *p*-bromophenylhydrazine was heated at 100°

in a pressure bottle for some hours, the solution filtered and evaporated, and the residue crystallised several times from alcohol. The p-*bromophenylhydrazone*, $C_{29}H_{22}O{:}N_2H{\cdot}C_6H_4Br$, was thus obtained in the form of short, colourless prisms, which were fairly readily soluble in alcohol: it melted at 168—169°. The following results were obtained on analysis:

0·2338 gave 0·6286 CO_2 and 0·1015 H_2O. C = 73·32; H = 4·82.
0·2653 ,, 0·0870 AgBr. Br = 13·95.
$C_{35}H_{27}ON_2Br$ requires C = 73·55; H = 4·73; Br = 14·01 per cent.

The *acetyl* derivative of tetraphenyl*cyclo*pentenolone was obtained by boiling it with excess of acetic anhydride for some hours, pouring the mixture into water, neutralising the acid with sodium carbonate, and extracting with benzene. On evaporation of the benzene, it separated in prisms of a dark reddish-purple colour. Repeated crystallisation from benzene, alcohol, and other solvents failed to remove the last traces of the colouring matter, but the crystals, although coloured, melted sharply at 218°, and the melting point was not altered by recrystallisation. The substance is easily soluble in benzene, but only sparingly so in alcohol. The following results were obtained on analysis:

0·2408 gave 0·7388 CO_2 and 0·1132 H_2O. C = 83·67; H = 5·22.
$C_{31}H_{24}O_3$ requires C = 83·78; H = 5·41 per cent.

*Action of Bromine, Phosphorus Pentachloride, and Alcoholic Hydrogen Chloride on Tetraphenyl*cyclo*pentenolone.*—When solutions of tetraphenyl*cyclo*pentenolone (5 grams) and of bromine (2 grams) in chloroform, all carefully dried, were mixed, hydrogen bromide was slowly evolved. The mixture was left under a bell jar along with a dish containing soda-lime until the reaction was completed, and on subsequent evaporation of the chloroform, small, dark red crystals were deposited. By recrystallisation from a mixture of benzene and light petroleum, the substance was obtained in colourless crystals, which were found to contain bromine, but no satisfactory analysis could be made because it is very unstable, decomposing at the ordinary temperature with evolution of hydrogen bromide. Such results as were obtained indicated that the substance was probably a monobromo-derivative of tetraphenyl*cyclo*pentenolone.

A colourless, crystalline product containing chlorine was formed by gently warming tetraphenyl*cyclo*pentenolone with phosphorus pentachloride, but it could not be purified for analysis on account of the readiness with which it decomposed. The same substance, or at least one which possessed the same appearance and properties, was produced by the action of alcoholic hydrogen chloride upon tetraphenyl*cyclo*pent-

enolone. This unstable compound was probably a monochloro-derivative of tetraphenyl*cyclo*pentenone, judging from the results of approximate estimations of the chlorine contained in it.

*Oxidation of Tetraphenyl*cyclo*pentenolone.*—Oxidation proceeded steadily when an acetic acid solution of chromium trioxide was slowly added to a concentrated solution of tetraphenyl*cyclo*pentenolone in glacial acetic acid, the mixture being kept cold during the process. The mixture was then poured into water, and the solid which separated was collected on a filter, washed with water, and finally warmed with a solution of sodium carbonate. A portion went into solution, but part remained undissolved in the sodium carbonate, and was removed by filtration. The alkaline solution was acidified and extracted with ether; on evaporation of the ether, crystals were deposited which were easily recognised as benzoic acid. The residue, insoluble in sodium carbonate, was crystallised from benzene, from which it separated in the form of colourless crystals melting at 164—165°. The substance, which is neutral in character, is readily soluble in benzene, but only very sparingly so in alcohol. The following results were obtained on analysis:

0·2049 gave 0·6035 CO_2 and 0·0877 H_2O. C = 80·32; H = 4·75.
0·1893 „ 0·5591 CO_2 „ 0·0806 H_2O. C = 80·55; H = 4·73.
$C_{28}H_{20}O_4$ requires C = 80·0; H = 4·76 per cent.

A determination of the molecular weight by the cryoscopic method, benzene being used as solvent, gave a result in conformity with the foregoing formula.

Wt. of substance.	Wt. of solvent.	Depression.	Mol. wt.	$C_{28}H_{20}O_4$ mol. wt.
0·1571	13·612	0·14°	404	420

The only substance of the formula $C_{28}H_{20}O_4$ which in any way resembles in physical properties the substance described above is *iso*benzil, $\begin{matrix}CPh\cdot O\cdot COPh\\ \|\\ CPh\cdot O\cdot COPh\end{matrix}$, of which the melting point is stated to be 159° (Klinger, *Ber.*, 1891, **24**, 1265).

When tetraphenyl*cyclo*pentenolone was heated on the water-bath with chromium trioxide, glacial acetic acid being used as solvent, the only product which could be detected was benzoic acid. Attempts were also made to oxidise tetraphenyl*cyclo*pentenolone with sodium hypobromite, but these were unsuccessful, no change taking place.

*Tetraphenyl*cyclo*pentenol.*

A mixture of 10 grams of tetraphenyl*cyclo*pentenolone, 15 grams of red phosphorus, and 60 c.c. of aqueous hydriodic acid (b. p. 126°) was boiled under a reflux condenser for 3 hours. After cooling, the acid

solution was poured off and the solid residue was ground in a mortar, thoroughly washed with water, and dried. The crude product was dissolved in benzene, and the solution agitated successively with aqueous sulphurous acid, aqueous sodium carbonate, and water, and then dried with calcium chloride. On concentration, nearly colourless crystals were obtained, the dark colouring matter present in the crude product being readily soluble in benzene. The substance, after purification by recrystallising several times from alcohol, afforded the following results on analysis:

0·2003 gave 0·6605 CO_2 and 0·1069 H_2O. C = 89·93; H = 5·92.
$C_{29}H_{24}O$ requires C = 89·69; H = 6·18 per cent.

The molecular weight was determined by the cryoscopic method, benzene being used as solvent.

Wt. of substance.	Wt. of solvent.	Depression.	Mol. wt.	$C_{29}H_{24}O$ mol. wt.
0·1537	15·223	0·13°	380	388

From these results, and from the properties of the substance described below, it is seen to be *tetraphenylcyclopentenol*. It crystallises from benzene, in which it is readily soluble, in colourless, lustrous needles, which melt at 162°. It is sparingly soluble even in boiling alcohol, and not at all readily soluble in ether. An alcoholic solution of this substance, rendered alkaline by the addition of a few drops of aqueous sodium carbonate, quickly changes the colour of potassium permanganate solution.

The same substance was obtained in a different way. Two grams of tetraphenyl*cyclo*pentenolone were dissolved in 10 grams of glacial acetic acid, 0·5 gram of red phosphorus and 0·25 c.c. of hydriodic acid were added, the mixture was boiled for three hours under a reflux condenser, and finally the product was separated and purified by the method already described.

We had expected to obtain tetraphenyl*cyclo*pentenone by reducing tetraphenyl*cyclo*pentenolone with hydriodic acid, and therefore we attempted to prepare an oxime and a hydrazone from the product. However, it could not be induced to react with either hydroxylamine, phenylhydrazine, or *p*-bromophenylhydrazine, in whatever way the conditions were modified. This fact, together with the other properties of the reduction product, led to the conclusion that the oxygen which it contained must be present in the form of a hydroxyl group, that is, it must be a tetraphenyl*cyclo*pentenol.

The *acetyl* derivative of tetraphenyl*cyclo*pentenol was prepared by heating it with fused sodium acetate and excess of acetic anhydride for some hours. The mixture was then poured into water and the insoluble ortion collected on a filter, washed with water, dried,

and crystallised from a mixture of benzene and alcohol. It crystallises in short, colourless, lustrous prisms, which melt at 181—182°. It is very readily soluble in benzene, but much less readily in alcohol. The following results were obtained on analysis:

0·2429 gave 0·7726 CO_2 and 0·1268 H_2O. C = 86·72; H = 5·80.
0·2236 „ 0·7126 CO_2 „ 0·1195 H_2O. C = 86·91; H = 5·94.
$C_{31}H_{26}O_2$ requires C = 86·51; H = 6·04 per cent.

Action of Bromine on Tetraphenylcyclopentenol.—Five grams of tetraphenyl*cyclo*pentenol were dissolved in chloroform and a solution of 2·3 grams of bromine in chloroform was added; the substances were all thoroughly dried before use. Hydrogen bromide was evolved at once and the reaction proceeded fairly rapidly. The mixture was left under a bell jar, which also contained soda-lime, until the action had ceased, the chloroform was then evaporated off, and the residue recrystallised from a mixture of benzene and light petroleum. After several crystallisations, *monobromotetraphenylcyclopentenol*, $C_{29}H_{22}Br{\cdot}OH$, was obtained in a state of purity. It forms colourless, prismatic crystals, which are easily soluble in benzene; its melting point is 215°.

0·1700 gave 0·0690 AgBr. Br = 17·27.
$C_{29}H_{23}OBr$ requires Br = 16·95 per cent.

Action of Phosphorus Pentachloride and of Alcoholic Hydrogen Chloride on Tetraphenylcyclopentenol.—When a mixture of tetraphenyl*cyclo*pentenol with the calculated quantity of phosphorus pentachloride was gently heated a vigorous action took place. The product was treated with water, and the insoluble portion dissolved in ether. On evaporation of the ether, dark red crystals were deposited, which were finally obtained free from colouring matter by repeated crystallisation from a mixture of benzene and light petroleum. Analysis showed the substance to be a *monochlorotetraphenylcyclopentene*. It crystallises in colourless prisms which melt at 181°. It is freely soluble in benzene and fairly so in alcohol, from which it can be crystallised without decomposition.

0·1685 gave 0·0599 AgCl. Cl = 8·79.
$C_{29}H_{23}Cl$ requires Cl = 8·72 per cent.

When tetraphenyl*cyclo*pentenol is treated with alcoholic hydrogen chloride, the same chlorine derivative of tetraphenyl*cyclo*pentene is obtained. About a gram of tetraphenyl*cyclo*pentenol was mixed with alcohol previously saturated with hydrogen chloride, and the mixture agitated at frequent intervals until the greater part of the solid had gone into solution. After some hours, the solution was filtered, the filtrate mixed with water, and the precipitated solid collected

and crystallised from alcohol. The crystals melted at 181°, and a mixture of them with the substance obtained by means of phosphorus pentachloride melted sharply at the same temperature.

Tetraphenylcyclopentene and Tetraphenylcyclopentane.

Tetraphenyl*cyclo*pentenol is reduced when heated in a sealed tube with hydriodic acid and red phosphorus, giving a mixture of two hydrocarbons in varying proportions. The temperature must be carefully regulated in order to obtain a satisfactory result; thus, up to 160° hydriodic acid had little or no action; at 210°, the product was a tarry mass, which did not invite further treatment; at 175°, a white powder mixed with a little of an oil was obtained; at a temperature of nearly 190° the oil was the chief product, and only a little of the white powder was present.

In order to obtain both the oily product and the white powder, the following conditions were finally adopted. Three grams of tetraphenyl*cyclo*pentenol, reduced to a fine powder, were mixed with 5·5 grams of red phosphorus and 30 grams of hydriodic acid (b. p. 126°), and the mixture was heated in a sealed tube at a temperature of about 180° for some hours. The product, after removal of the acid liquid, was crushed to powder, thoroughly washed with water, dried, and then extracted first with boiling ether and next with boiling benzene. The ether dissolved all of the white powder, but only a little of the oily substance, which is sparingly soluble in that solvent; the benzene extract contained the greater part of the oily substance. Each extract was agitated successively with aqueous sulphurous acid, aqueous sodium carbonate, and water, and then dried with calcium chloride. From the ethereal solution a white powder was obtained on distilling off the ether; this substance was purified by recrystallisation from ether, from which it separates as a white, crystalline powder. It melts with decomposition above 300°, and is easily soluble in benzene but only very sparingly so in alcohol. Analysis showed that it is a hydrocarbon of the formula $C_{29}H_{24}$, and in all probability the unsaturated compound, 1 : 2 : 4 : 5-*tetraphenylcyclopentene*.

0·1379 gave 0·4721 CO_2 and 0·0806 H_2O. C = 93·37; H = 6·49.
$C_{29}H_{24}$ requires C = 93·55; H = 6·45 per cent.

On evaporation of the benzene solution, the other hydrocarbon was obtained in an oily condition, but it separated in crystals from a mixture of alcohol and acetone. It melts at 80·5—81°, which is the melting point given by Wislicenus (*loc. cit.*) for 1 : 2 : 4 : 5-tetraphenyl*cyclo*pentane.

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CXXXIV.—*The Form of Change in Organic Compounds, and the Function of the a-Meta-orientating Groups.*

By Arthur Lapworth.

In a paper published in the Transactions of the Society some time ago (Trans., 1898, 73, 445), the author showed that a very large number of changes and interactions in organic chemistry could be represented by forms, deducible from two simple types, which may be termed the $\alpha\gamma$- and $\alpha\beta$-rules. A critical examination of what is really essential to the applicability of these rules shows that the whole matter rests solely on the assumption that isomeric change is due, not to mere interchange of the position of atoms or groups in a molecule, but in general to a series of migrations, apparent or real, and that only one atom or group migrates at a time. With such an assumption, it is easy to show that there is no way of avoiding the conclusion that if the production of ring compounds is excluded and no change of valency occurs, the migration must be representable by a strict application of the $\alpha\gamma$-rule; if, on the other hand, change of valency does occur at any part of the molecule, then the $\alpha\beta$-rule must come into play at that point. It is of no consequence how the migration is effected, as the principle simply precludes a direct interchange of groups, and the representation of undissociated compounds by illegitimate formulæ. The author was greatly influenced by the apparent simplicity of the stereochemical view of the mode of transference suggested in his first paper (pp. 448 and 452), but is no longer able to regard explanations based on such principles as of any real value.

Occasion has already been taken to point out (Proc., 1901, 17, 2) that in applying the author's $\alpha\gamma$- and $\alpha\beta$-rules, the intermediate positions which were assigned to a migratory group in its transference must not be regarded as real resting points, but rather as representing the various possible positions of the group in the line between its initial and final positions of attachment.

An explanation which appears capable of explaining, amongst other things, the very general applicability of the rules is one based on the assumption that change in organic chemistry is largely due to the occurrence of a dissociation between singly bound groups and subservient to the following law; *the state of dissociation between two singly bound atoms which leads to isomeric change, exists only once in the molecule at any instant.*

A dissociation of the character which the above conception demands is found in weak electrolytes, and, in the author's opinion,

it is to electrolytic dissociation, often doubtless in extremely minute amount, that the majority of changes in organic compounds may be most probably assigned. This view, which the author has now held for a long time, and arrived at from a consideration of the prevalent forms of change, receives support in the recent appearance of the papers of Euler (*Ber.*, 1900, 33, 3202) and of Zengelis (*Ber.*, 1901, 34, 198), who, apparently from entirely different considerations, have been led to put forward a similar suggestion with regard, more particularly, to the hydrolysis of esters and sugars.

On this principle, the simplest possible case of isomeric change may be imagined to consist in the dissociation of a molecule X·Y at a point between two singly bound atoms into two groups, $\dot{X}$ and $\dot{Y}$, each of which is capable of becoming attached to one univalent atom or group to form an undissociated chemical molecule capable of free existence. The groups $\dot{X}$ and $\dot{Y}$ will, as a rule, be oppositely charged ions. Now the principle governing the possible modes in which $\dot{X}$ and $\dot{Y}$ may again become mutually attached appears to be that the resulting, now undissociated, molecule X·Y shall be immediately representable by a legitimate formula through a mere adjustment of the conventional "bindings."*

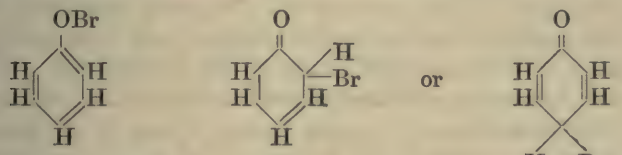
In order to avoid misconception, it must be pointed out that this adjustment takes place in general along an already existing line between the initial and final positions of mutual attachment of one group to another, a single binding becoming a double one, a double one a treble one, or *vice versâ*, or a single binding may altogether disappear. The converse of the last change, namely, the formation of a single binding where none existed before, is probably to be found only in cases where the formation of ring compounds is thereby involved; even here, however, it usually appears possible to trace exactly similar laws.

It should be made clear that the dissociation of X·Y may be followed, not by a reunion of $\dot{X}$ and $\dot{Y}$, but, in presence of other dissociated groups, by the union of these groups with others to form compounds which are not isomeric with the original substance.

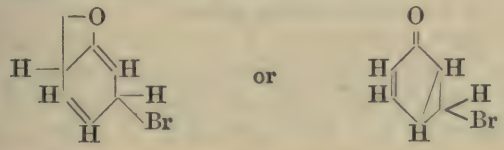
To illustrate the application of the preceding principles, a case of substitution, namely, the action of bromine on phenol, which appears to

* Possibly the formation of the new compound is preceded by an actual readjustment of the bindings in the molecule. Thus it is probable, for instance, that a dissociated group $\dot{A}$·B:C·D:E may change to A:B·$\dot{C}$·D:E or A:B·C:D·$\dot{E}$, so that the $\alpha\gamma$- and $\alpha\beta$-rules and their stereochemical explanations may apply to the alteration of the position of free affinity in the dissociated group, and these changes may be successive, although no intermediate compounds are formed.

be fairly simple, may be considered. The bromine may be imagined to dissociate slightly into $\overset{+}{Br}$ and $\overset{-}{Br}$, and the weakly acid phenol as usual into $\overset{+}{H}$ and $O\cdot\overset{-}{C_6H_5}$, the bromination consisting in the union of $\overset{+}{Br}$ and $O\cdot\overset{-}{C_6H_5}$, the possible products are those in which these two groups (otherwise preserving their original characteristics so far as the relative positions of atoms contained in each are concerned) are mutually attached, so that by merely altering, if necessary, the bindings in the above-mentioned sense, a legitimate formula is at once obtained for the compound C_6H_5OBr. This is possible at the oxygen atom, at the carbon atoms 2- and 4-, but not at the carbon atoms 1- or 3-. The possible products are therefore:



unless it is supposed that ring compounds such as:



might be produced, a possibility which is sufficiently remote to require no further remarks.

The law relating to dissociated groups may be stated more strictly than on p. 1265 as follows. *The ions of organic compounds usually possess only one point of free valency*, which is merely another way of stating that they are usually weak electrolytes, and therefore form only univalent ions.

Following out the recently advanced conceptions of Abegg and Bodländer (*Zeit. anorg. Chem.*, 1899, 20, 453), a complex ion may be considered to arise from the union of a simple ion with a neutral component, and, conversely, a complex ion may break down into a simpler one and a neutral component. It should follow, therefore, that a molecule, X·Y·Z, may become dissociated into ions, say, X and Y·Z, and that afterwards the ion Y·Z may become further simplified into a neutral component Y and the ion Z, the latter carrying away the free affinity and the charge. A law similar to that just formulated will hold for the latter process, namely, that the neutral component Y shall be at once representable by a legitimate formula through an adjustment of the bindings in the sense already explained.

It will follow in general that a simple ion will be the more readily eliminated from a complex ion of a given type if it has a large "electroaffinity" (Abegg and Bodländer, *loc. cit.*), and it may be pointed out here that, in most simple cases where two groups are withdrawn from a molecule, the product of their union is a recognised electrolyte.

In illustration of this point, the author's conception of the breaking down of acetone cyanohydrin, $CN\cdot CMe_2\cdot OH$, under the influence of alkali may be alluded to. Here the dissociation probably occurs first between the hydrogen atom and the oxygen of the hydroxyl group, since it must in any case be supposed that all alcohols are feebly dissociated in this way. The ions are therefore $\overset{+}{H}$ and $CN\cdot\overset{-}{C}Me_2\cdot\dot{O}$, and in the negatively charged ion the CN group is known to have a large electroaffinity for the negative charge; it is, moreover, in such a position that its removal will result in the formation of a molecule at once representable by the legitimate formula $CMe_2{:}O$. The function of the alkali is doubtless to provide hydroxyl ions in the presence of which the concentration of the hydrogen ions of the cyanohydrin is greatly diminished, and the dissociation of the cyanohydrin consequently raised to a corresponding extent.

With this brief introduction, it is possible to proceed to some special cases to which these principles apply, and, in order to be able to deal generally with some of these, the following rule, easily deducible from what has been said, may be stated. *If, during a reaction, a group* $\dot{X}$ *might be expected to unite with an atom* R_α *in the complex* $\dot{R}_\alpha\cdot R_\beta{:}R_\gamma$, *then the product may contain, not only substances with the complex* $R_\alpha X\cdot R_\beta{:}R_\gamma$, *but also, and, sometimes exclusively, those with* $R_\alpha{:}R_\beta\cdot R_\gamma X$ *and their tautomeric forms.*

Some important forms of interaction may be at once mechanically deduced from the expansion of the simplest type of addition at a double binding, $A{:}B + X\cdot Y = AX\cdot BY$, and it is easy to show that the general equations may be true if read in either sense.

Firstly, expanding B we obtain:

$$A{:}B_\alpha\cdot B_\beta{:}B_\gamma + \dot{X} + \dot{Y} \longleftrightarrow AX\cdot\dot{B}_\alpha\cdot B_\beta{:}B_\gamma + \dot{Y} \longleftrightarrow AX\cdot B_\alpha{:}B_\beta\cdot\dot{B}_\gamma Y \quad (R),$$

easily seen to be the form to which so much importance has been attached by Thiele.

Secondly, expanding Y only:

$$A{:}B + \dot{X} + \dot{Y}_\alpha\cdot Y_\beta{:}Y_\gamma \begin{matrix} \swarrow AX\cdot\dot{B} + \dot{Y}_\alpha\cdot Y_\beta{:}Y_\gamma \\ \searrow \dot{A}\cdot B\cdot Y_\gamma\cdot Y_\beta{:}Y_\alpha + \dot{X} \end{matrix} \begin{matrix} \searrow \\ \swarrow \end{matrix} AX\cdot B\cdot Y_\gamma\cdot Y_\beta\,\dot{Y}_\alpha \quad (S).$$

This form is not translatable in terms of Thiele's rule, but is one

which will probably be found to be the basis of many reactions as yet imperfectly understood, and one or two cases where it appears directly applicable may be discussed. It is, no doubt, the type of change involved in the Claisen reaction in its simplest form, as, for example, when sodium ethoxide acts on a mixture of acetone and ethyl oxalate, a condensation which is perhaps the result of the following series of changes.

The ions $\overset{+}{\dot{N}a}$ and $CH_2{:}\overset{-}{C}Me{\cdot}\dot{O}$ of the sodium derivative of acetone, $CH_2{:}CMe{\cdot}ONa$ (Freer, *Amer. Chem. J.*, 1891, **13**, 322), unite with a carbonyl group of the ethyl oxalate. As sodium shows very little tendency to form complex ions, it is perhaps the negative ion which first becomes attached to the ethyl oxalate (compare, however, Proc., 1901, **17**, 95):

$$\dot{N}a + CH_2{:}CMe{\cdot}\dot{O} + O{:}C(OEt){\cdot}CO_2Et \longleftrightarrow \dot{N}a + \dot{O}{\cdot}C(OEt)(CO_2Et){\cdot}CH_2{\cdot}CMe{:}O.$$

The components on the right are the ions of the sodium compound, $NaO{\cdot}C(OEt)(CO_2Et){\cdot}CH_2{\cdot}CMe{:}O$, which, by loss of alcohol, affords the stable sodium compound, $NaO{\cdot}C(CO_2Et){:}CH{\cdot}CMe{:}O$, as the actual product.

As anything like an adequate discussion of the details of this reaction would occupy a very large amount of space, the author confines himself at present to the foregoing remarks.

The reaction between aldehydes and the metallic derivatives of *iso*-nitro-compounds doubtless proceeds in accordance with this type. Thus with potassium *iso*nitropropane and formaldehyde,

$$\dot{K} + \dot{O}{\cdot}NO{:}CMe_2 + CH_2{:}O \longleftrightarrow \dot{K} + O{:}NO{\cdot}CMe_2{\cdot}CH_2{\cdot}\dot{O} \longleftrightarrow O{:}NO{\cdot}CMe_2{\cdot}CH_2{\cdot}OK.$$

Thirdly, expanding both B and Y, we obtain the form thus roughly expressed:

$$X{\cdot}Y_\alpha{\cdot}Y_\beta{:}Y_\gamma + A{:}B_\alpha{\cdot}B_\beta{:}B_\gamma \longleftrightarrow AX{\cdot}B_\alpha{:}B_\beta{\cdot}B_\gamma{\cdot}Y_\gamma{\cdot}Y_\beta{:}Y_\alpha \quad \ldots\ldots \text{(T)}.$$

This doubtless includes, amongst others, the cases of interaction of $\alpha\beta$-unsaturated esters and ketones with ethyl sodio-malonate, -cyanoacetate, and -acetoacetate. Thus with methyl acrylate and ethyl sodiocyanoacetate:

$$Na{\cdot}O{\cdot}C(OEt){:}CH{\cdot}CN + O{:}C(OMe){\cdot}CH{:}CH_2 \longrightarrow Na{\cdot}O{\cdot}C(OMe){:}CH{\cdot}CH_2{\cdot}CH(CN){\cdot}C(OEt){:}O.$$

In his first paper, dealing with the subject of isomeric change (*loc. cit.*, p. 455), the author referred briefly to the case of *meta*-substitution

in the benzene series, using the case of the sulphonation of nitrobenzene by way of illustration, and showed that the most probable mode in which the change might be supposed to occur was that the acting agent united in the first instance with the side group, and that elimination of a substance then took place by removal of a hydrogen atom in the nucleus (necessarily the *meta*-atom, unless it is supposed that ring compounds like those depicted on p. 1267 are produced) with a group attached to the side chain. The initial stages were mostly similar to those usually assumed to take place when nitromethane, for example, is converted into a salt of its *iso*-form by a metallic hydroxide; subsequently, in the benzene derivative, the hydrogen atom is removed, not from the α-position, but from the related γ-position. That is to say, the benzene compound was supposed to be converted into a derivative of its tautomeric form corresponding with the *iso*-forms of fatty nitro-compounds, and this was then converted into the *meta*-substitution derivative by isomeric change in accordance with the $\alpha\gamma$-rule. The first actions assumed, written in the usual form, may be compared thus:

(1) Caustic potash acting on a fatty nitro-compound,

$$:CH\cdot NO:O + HOK \longrightarrow :CH\cdot NO\begin{matrix}OH\\OK\end{matrix} \longrightarrow :C:NO\cdot OK + HOH.$$

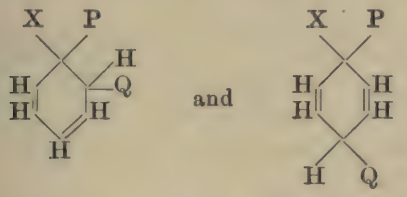
(2) Sulphuric acid acting on nitrobenzene ($S=SO_3H$),

$$\cdot CH\cdot\dot{C}:\dot{C}\cdot NO:O + HOS \longrightarrow :CH\cdot\dot{C}:\dot{C}\cdot NO\begin{matrix}OH\\OS\end{matrix} \longrightarrow$$
$$:C:\dot{C}\cdot\dot{C}:NO\cdot OS + HOH$$

It was not perceived at the time when this view was put forward that, if there be any truth in the conception, then those groups which, in the aromatic series, are the characteristic *meta*-orientating groups should be capable of reacting on the tautomeric *normal* and *iso*-forms $>CH\cdot R$ and $>C:RH$ when in attachment to a $>CH$ group. The fact that the groups, NO_2, $CO\cdot R$, and CN, do possess both properties is at least very striking (compare Hantzsch and Veit, *Ber.*, 1899, 32, 607, and Hantzsch and Osmund, *ibid.*, 341), and as regards the only other *meta*-orientating group, namely, $SO_2\cdot R$, the experiments of Kötz (*Ber.*, 1900, 33, 1120) are sufficient to show that its properties are similar to those of the other three groups, more especially as it was found that the compound $Ph\cdot SO_2\cdot CH(SO_2Et)_2$ behaved as a strong acid. It may be remarked that the foregoing groups in the fatty series render the α-hydrogen atom, and in the benzene series the related γ-hydrogen atom, replaceable, so that it appears probable that the formation of large quantities of *meta*-di-derivatives is due in general to the occurrence of changes very similar to those occurring in the fatty series, the relationship being expressed by the $\alpha\gamma$-rule.

It may be argued that substitution by direct attack in the nucleus is possible, and that therefore *meta*-derivatives may be formed in this way. Doubtless they are thus produced to a certain extent in all cases; nevertheless, it seems impossible to believe that such widely different groups as $N(CH_3)_2$, CH_3, Cl, and CH_2Cl, should render the *ortho*- and *para*-hydrogen atoms directly replaceable, and that the others, NO_2, CN, &c., should have precisely the opposite effect by a mere exertion of an attractive or repulsive influence. In the author's opinion, so far as direct substitution in the nucleus is concerned, all groups may be presumed to have an *ortho-para*-orientating influence, due, perhaps, to considerations like those suggested by Thiele, and the formation of *meta*-substitution derivatives in quantities preponderating over those of the *ortho*- and *para*-derivatives combined, must be attributed to an entirely different phenomenon.

The formation of *ortho*- and *para*-substitution products simultaneously from an ordinary benzene mono-substitution derivative $C_6H_5{\cdot}X$ by an agent PQ is perhaps due to the formation of intermediate compounds of the types



related by the $a\gamma$-rule, and yielding by loss of HP the benzenoid *ortho*- and *para*-derivatives, C_6H_4XQ. In consequence, were X of a nature capable of exerting a steric hindrance on the formation of such an intermediate compound, the action would be hindered, but without, of course, preventing the *para*-hydrogen atom from being removed as easily as the *meta*-atom. If, therefore, in the fatty series, the group $X{\cdot}\dot{C}{:}\dot{C}$ forms additive products with difficulty, then it is to be expected that substitution in the compound $C_6H_5{\cdot}X$ will also be difficult. Such an example is found in *tert.*butylbenzene.

Since, then, it appears that the function of the characteristic *meta*-orientating groups in the benzene series is probably quite similar to that which they exercise in the fatty series, it should follow that the similarity could be traced, not only in the effect which they exercise in the simplest cases of substitution, but in more complex reactions. One of these, applicable to many fatty compounds in which they occur, is the Claisen reaction, the course

of which has already been discussed (p. 1269). Now, in order that this action may occur, it is necessary that two hydrogen atoms should be present at the α-carbon atom, and it happens that in benzenoid ketones, esters, &c., where the carbonyl group is in direct attachment to the nucleus there is no hydrogen at the α-position; proceeding, therefore, to the related point, the γ-position, only one hydrogen atom is present as a rule, namely, the *meta*-hydrogen atom, but in some cases there is a stable CH_2 group at the γ- or γ'-position outside the ring. Such a substance is found in *o*- or *p*-methylbenzophenone or ethyl *o*- or *p*-toluate, but not in the corresponding *meta*-derivatives.

Whilst these compounds react only with the greatest difficulty, if at all, those containing the more reactive nitro-group, as, for example, *o*- and *p*-nitrotoluenes, are capable of taking part in the Claisen reaction. Thus Reissert found (*Ber.*, 1897, **30**, 1030) that the methyl group in these two compounds was attacked, but that no reaction occurred in the case of the *meta*-nitrotoluene; he asserts, also, that ethyl oxalate is the only ester which can be used. The author has confirmed Reissert's statement regarding the inactivity of the *meta*-compound, but has found that amyl nitrite may be used in place of ethyl oxalate, and yields the oximes of *o*- and *p*-nitrobenzaldehydes; no doubt other esters might also be used, provided that the product were a sufficiently stable sodium derivative. The reaction is evidently a particular case of γ- or *meta*-substitution, in which the *meta*-position is outside the ring, that in the ring being excluded from the type of reaction.

It may be supposed, as in other cases, that a compound of the type $CH_2{:}\dot{C}{\cdot}\dot{C}{:}NO{\cdot}ONa$ is produced, having a constitution analogous to that of the quinoneoximes on the one hand, and to the *iso*sulphate of nitrobenzene (p. 1270) on the other. The *iso*-derivative then reacts with ethyl oxalate, as follows (compare p. 1269):

$$\begin{array}{l} CO_2Et{\cdot}C(OEt){:}O \\ CH_2{:}\dot{C}{\cdot}\dot{C}{:}NO{\cdot}ONa \end{array} \longrightarrow \begin{array}{l} CO_2Et{\cdot}\dot{C}(OEt){\cdot}ONa \\ \quad\vdots \\ CH_2{\cdot}\dot{C}{:}\dot{C}{\cdot}NO{:}O \end{array} \longrightarrow$$

$$\begin{array}{l} CO_2Et{\cdot}\dot{C}{\cdot}ONa \\ \quad\vdots\vdots \\ CH{\cdot}\dot{C}{:}\dot{C}{\cdot}NO{:}O \end{array} + EtOH;$$

that is, in accordance with the reaction expressed by $A{:}B + X{\cdot}Y$, in which Y is expanded twice.

As such a reaction should, in turn, be applicable to similarly constituted fatty compounds, it seemed that it might be possible to condense ethyl oxalate, &c., with open chain substances of the type $\cdot CH_2{\cdot}CR{:}CR{\cdot}X$ ($X = NO_2$, CN, SO_2R, $CO{\cdot}R$) at the γ-position instead of at the α-position, as usual.

Compounds of the above type and containing no α-hydrogen atom are difficult to obtain in large quantities. Experiments were most successful with ethyl crotonate, and the results justify the prediction, as ethyl γ-oxalocrotonate may be obtained, under the proper conditions, in fairly large amount. It is a matter of little difficulty to trace the course of the reaction in the above manner.

The number of possible condensation products in such cases, and the fact that some of them may be formed with greater ease than the γ-oxalo-derivatives, may obviously render the isolation of the latter a matter of great difficulty.

That the ethyl oxalocrotonate is not the α-derivative is shown by the marked difference between its properties and those of other α-oxalo-esters and ketones. It affords a black instead of the red to violet coloration with ferric chloride which α-derivatives usually give, and its stability towards hydrolytic agents is incomparably greater than that of such compounds; whilst the α-oxalo-esters decompose into oxalic acid on the one hand, and pyruvic acids and carbon dioxide on the other, the new substance does neither; when boiled with alkalis, it gives no oxalic acid, and with acids it suffers hydrolysis and the product loses water, being converted into a substance which is evidently a ring compound, $CH\begin{matrix}CH{=}C\\ CH{\cdot}CO\end{matrix}\!\!>\!O\!-\!CO_2H$, a change which would be impossible with an α-oxalocrotonic ester. Finally, the idea that the substance might be a β-oxalo-ester may be at once set aside, as it is impossible to find a suitable formula for such a substance.

The condensation of ethyl crotonate with ethyl oxalate in the above way might, at first sight, be attributed to the presence of the group $CH_3{\cdot}\dot{C}{:}C{\cdot}$, but that this is not the case is shown by several facts. Thus ethyl α-methylacrylate, which is isomeric with ethyl crotonate and contains that group, gives no indication of forming a similar compound. Again, other unsaturated esters containing the grouping $\cdot CH_2{\cdot}CR{:}CR_2$ should behave in a similar way, but examination of the ester of camphorenic acid, which also contains this grouping, showed that no condensation occurred. The power of two such pairs of doubly-bound carbon atoms in attachment to a CH_2 group to render the reaction a possible one is unquestionable (Thiele, *Ber.*, 1900, 33, 666), but with those substances which contain only one such pair, there is almost certainly a sharp line of demarcation, both in the fatty and in the aromatic series, between the two classes represented respectively by the formulæ $\cdot CH_2{\cdot}\dot{C}{:}\dot{C}{\cdot}$ and $\cdot CH_2{\cdot}\dot{C}{:}\dot{C}{\cdot}X$ (where X = CO, &c.).

Experimental.

Action of Sodium Ethoxide and Amyl Nitrite on o- *and* p-*Nitrotoluenes.*

Amyl nitrite has little or no action on *o*- or *p*-nitrotoluene in presence of alcoholic sodium ethoxide, but if the anhydrous ethoxide is used there is little difficulty in isolating the oxime of *o*- or *p*-nitrobenzaldehyde respectively from the product. The mode of treatment found most suitable was as follows.

Sodium (2—3 grams) was dissolved in 12 times its weight of alcohol, and the excess of the latter afterwards got rid of by distillation in a stream of hydrogen at about 180°, the removal being completed in a vacuum at this temperature. The residue was covered with about 200 c.c. of thoroughly dried and purified ether, and a mixture of amyl nitrite and *o*-nitrotoluene was then slowly poured in, the temperature being at first kept down by means of a freezing mixture. The whole, after remaining a few days at the ordinary temperature, was poured on crushed ice, the resulting aqueous solution being separated, extracted twice with pure ether, and freed from the latter by a current of air. On adding dilute hydrochloric acid to the solution, a fairly copious precipitate of solid matter separated. This was collected, dried, and crystallised from benzene.

0·2097 gave 0·3878 CO_2 and 0·0710 H_2O. C = 50·4; H = 3·8.
$C_7H_6O_3N_2$ requires C = 50·7; H = 3·7 per cent.

The substance melted at 95—96° and had all the appearance and properties of *o*-nitrobenzaldoxime. In order to complete its indentification, it was heated for some time with concentrated hydrochloric acid, the liquid being then extracted with ether and the latter evaporated. A residue of solid matter remained, which had the properties of *o*-nitrobenzaldehyde, and on dissolving it in dilute acetone and adding a few drops of dilute sodium hydroxide, rapid darkening ensued, followed by a deposition of indigo.

With *p*-nitrotoluene, the yield of oxime is not so good, but no difficulty was experienced in isolating it. The crystalline substance obtained melted at 128—129°, and when heated with pure *p*-nitro benzaldoxime, its melting point was not depressed. On analysis:

0 1505 gave 0·2780 CO_2 and 0·0515 H_2O. C = 50·3; H = 3·8 per cent.

With *m*-nitrotoluene, no evidence of the formation of an oxime could be obtained, and no positive result ensued, even when in this case ethyl oxalate was substituted for amyl nitrite. As condensation with ethyl oxalate almost invariably takes place more readily than with

amyl nitrite, it may be concluded that *m*-nitrotoluene behaves altogether differently from the *o*- and *p*-compounds in this regard.

Experiments were made in which amyl and ethyl formates and nitrates were substituted for oxalates and nitrites. With the formates, reaction certainly occurs, but on treating the product from *o*-nitrotoluene with water, a crystalline, neutral compound separates, and only a small quantity of any acid substance could be detected. The neutral substance crystallised from alcohol in nearly colourless prisms melting at 121°, and gave the following results on analysis :

0·1148 gave 0·2577 CO_2 and 0·0492 H_2O. C = 61·2 ; H = 4·7.
$C_{14}H_{12}O_4N_2$ requires C = 61·7 ; H = 4·4 per cent.

The substance was identified as 2 : 2′-dinitrodibenzyl,

$$C_6H_4(NO_2)\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

which, it is interesting to note, has been obtained only on one previous occasion, namely, on treating *o*-nitrophenylpyruvic acid, the product from *o*-nitrotoluene, ethyl oxalate and sodium ethoxide, with alkali (Reissert, *Ber.*, 1897, 30, 1039). As the substance is not formed when ethyl formate is omitted in the above reaction, it appears highly probable that it owes its origin to a condensation product of *o*-nitrotoluene and ethyl formate, which, judging from the properties of *p*-nitrophenylacetaldehyde, would be a highly unstable substance (Lipp, *Ber.*, 1886, 19, 2647).

Experiments with other o- *and* p-*Substituted Toluenes.*—In endeavouring to extend the above observations, ethyl *o*- and *p*-toluates were treated with ethyl oxalate and sodium ethoxide under several conditions. Here it was found that small quantities of unstable, acidic substances were produced which were ketonic in their nature and gave blue to violet colorations with ferric chloride. These substances were possibly the condensation products sought for, but good numbers were not obtained when they were analysed, owing to the small quantities hitherto isolated, and the consequent difficulty of ensuring their purity. With *o*- and *p*-toluonitriles, violent reactions took place, but rapid decomposition ensued, black, amorphous masses being deposited, and this occurred also in absence of ethyl oxalate.

It is hoped that further experiments with *o*- and *p*-methylsulphones and ketones will give more definite results. In none of these cases, however, is it to be expected that such definite results will be obtained as with the compounds containing the highly reactive nitro-group.

Condensation of Ethyl Crotonate with Ethyl Oxalate. Formation of Ethyl γ-Oxalocrotonate, $CO_2Et{\cdot}C(OH){:}CH{\cdot}CH{:}CH{\cdot}CO_2Et$.

Ethyl crotonate and ethyl oxalate condense in presence of anhydrous sodium ethoxide suspended in ether or toluene. The liquid slowly becomes bright yellow in colour as the ethoxide dissolves, and after the lapse of a week, a yellow, microcrystalline deposit settles on the walls of the containing vessel. A considerable quantity of the product remains dissolved, however, and the whole should be poured into ice-water containing an excess of dilute acetic acid, the ethereal solution separated, washed, and extracted repeatedly with dilute sodium carbonate. The crude ester may be isolated by acidifying the alkaline extract with acetic acid and extracting with ether, which should afterwards be allowed to evaporate spontaneously.

The oxalo-derivative may also be obtained by adding a mixture of the two esters to the calculated quantity of sodium, cut into thin sheets, and covered with a considerable quantity of absolute ether. In all cases, the presence of a very small quantity of water is sufficient to completely prevent the formation of the desired product, and the yield never exceeds 40 per cent. of the theoretical amount.

The ester is best purified by dissolution in cold dilute sodium carbonate, powdered sodium acetate being afterwards added to the solution. The sodium compound then separates as a voluminous mass of needles which may be separated by filtration, washed with dilute sodium acetate solution, and afterwards decomposed by dilute hydrochloric acid. The nearly white ester which separates is dried, and crystallised from a mixture of benzene and light petroleum. A specimen of the ester was analysed.

0·2265 gave 0·4684 CO_2 and 0·1336 H_2O. C = 56·4; H = 6·6.
$C_{10}H_{14}O_5$ requires C = 56·0; H = 6·6 per cent.

Ethyl γ-oxalocrotonate is a nearly colourless solid. It dissolves very readily in all organic media with the exception of light petroleum in which it is sparingly soluble, even when hot; it is nearly insoluble in water. It crystallises from a mixture of ethyl acetate and light petroleum in small, transparent prisms, and from light petroleum in fan-shaped aggregates of plates or isolated, short, compact prisms or tablets. When these are examined in convergent polarised light, an optic axis of a biaxial interference figure is seen to emerge obliquely with regard to the field.

When melted on a glass slip beneath a cover-glass, it solidifies suddenly on cooling in bundles of fine needles interspersed with irregularly arranged patches of indistinct crystalline structure.

That the ester exists in the enolic form,

$$CO_2Et\cdot C(OH):CH\cdot CH:CH\cdot CO_2Et,$$

is shown by the fact that it is a fairly strong acid; it expels carbon dioxide rapidly from dilute solutions of sodium carbonate, and if a moderately strong solution is made, the yellow sodium derivative crystallises out. From its solution in alkali, the ester is precipitated on addition of acetic acid. The presence of the enolic grouping in the substance is also shown by the fact that its dilute alcoholic solution is coloured an intense brownish-black on addition of ferric chloride, and this coloration is not discharged by the addition of a very large excess of strong mineral acid; with ferrous sulphate, no marked coloration is produced.

Attempts to prepare the acetyl and benzoyl derivatives of the ester resulted in the formation of white, amorphous masses, which did not dissolve at once in dilute sodium carbonate solution. They were slowly decomposed by water and moist solvents, however, and could not be made to crystallise.

The ester cannot be purified by distillation, even under reduced pressure, as it rapidly decomposes; it boils at 180° under the ordinary pressure, losing a certain amount of alcohol, and affording, for the most part, a carbonaceous mass. A small quantity of an oily substance distils over and a phenolic odour becomes apparent, but the majority of the distillate is probably the ester of the coumalincarboxylic acid described later.

On warming the compound with soda, it dissolves rapidly, and if the alkali be strong, separation of a red, oily sodium salt ensues. The salt dissolves on shaking, however, and the solution becomes intensely yellow. On acidifying the diluted liquid after boiling for a considerable time, little or no oxalic acid could be detected when the highly purified ester was used. When hot hydrochloric acid is used in the hydrolysis, the liquid, at first slightly yellow, becomes colourless as the substance dissolves, and here again no carbon dioxide or oxalic acid could be detected as a product of decomposition.

When the substance is warmed with solutions of aniline, or hydrazines in dilute acetic acid or in alcohol, yellow precipitates are slowly produced; the aniline derivative is readily obtained in a crystalline form, but has not as yet been closely examined.

The molecular weight of ethyl oxalocrotonate in acetic acid was determined by the cryoscopic method. The mean of three concordant measurements was 225, the number calculated for a substance having the formula $C_{10}H_{14}O_5$ being 214.

Action of Sodium Ethoxide on a Mixture of Ethyl β-Ethoxybutyrate and Ethyl Oxalate.

In order to obtain evidence as to whether the compound

$$CH_3{\cdot}CH(OEt){\cdot}CH{:}C(OEt){\cdot}ONa$$

might be regarded as a probable step in the formation of ethyl oxalocrotonate, sodium ethoxide was allowed to act on a mixture of ethyl β-ethoxybutyrate and ethyl oxalate under the conditions found to be most advantageous for the production of that substance.

It was found that it was easy to obtain some quantity of ethyl oxalocrotonate in this way, but the yield, as compared with that obtained directly from ethyl crotonate, was small, and it is probable that the compound $CH_3{\cdot}CH{:}CH{\cdot}C(OEt)_2{\cdot}ONa$ is the true intermediate substance if any such is produced at all, although it is manifestly impossible to determine this with any degree of certainty.

The *sodium* derivative of ethyl oxalocrotonate,

$$CO_2Et{\cdot}C(ONa){:}CH{\cdot}CH{\cdot}CO_2Et,$$

is formed when the ester is dissolved in sodium carbonate or sodium hydroxide solution. It is not very readily soluble in cold water, and quite sparingly so in solutions of more soluble sodium salts. It forms long, yellow needles which have straight extinctions in polarised light, their directions of greatest length and elasticity being coincident. A specimen crystallised from a solution of sodium acetate was washed with water and analysed after drying over sulphuric acid in a vacuum.

0·3962 gave 0·1143 Na_2SO_4. Na = 9·4.

$C_{10}H_{13}O_5Na$ requires Na = 10·0 per cent.

When this substance is washed with ether which has not been specially dried, it slowly decomposes and the ether on evaporation yields the nearly pure ester, indicating that the substance is hydrolytically decomposed by water to a very considerable extent.

The *copper* derivative, $(C_{10}H_{13}O_5)_2Cu$, is produced when an aqueous solution of copper acetate is added to the ester dissolved in alcohol; the blue solution of the copper salt becomes yellowish-green, and finally an amorphous greenish-brown precipitate is formed, which may be separated and washed with dilute alcohol. It is soluble in alcohol or ether, and could not be obtained in a crystalline condition; on treatment with acids, it yields the pure ester. A specimen, after drying at 100°, was analysed:

0·3635 gave 0·634 CuO. C = 12·8.

$C_{20}H_{26}O_{10}Cu$ requires Cu = 12·9 per cent.

With dilute aqueous solutions of the sodium derivative, solutions of soluble calcium, barium, nickel, or cobalt salts give no precipitates;

mercuric chloride throws down a bulky precipitate insoluble in ether. In somewhat concentrated solutions, calcium chloride forms a white, flocculent precipitate insoluble in ether; the *silver* compound is precipitated on adding silver nitrate, but rapidly darkens in the light, depositing metallic silver.

γ-Oxalocrotonic Acid, $CO_2H{\cdot}C(OH){:}CH{\cdot}CH{:}CH{\cdot}CO_2H$.

This substance may be obtained in small quantities by the following process. The sodium derivative of the diethyl ester is finely powdered and triturated in a mortar with a 30 per cent. solution of sodium hydroxide, the liquid being added in small quantities and the temperature kept low. The solution, which is reddish-yellow in colour, is allowed to remain at the ordinary temperature for several hours until a small quantity, when diluted and acidified with acetic acid, gives no precipitate. The whole is then diluted with several times its bulk of water, cooled in ice, acidified with a large excess of sulphuric acid, and extracted about 20 times with ether, the latter being dried over calcium chloride and evaporated.

The substance may be purified by crystallisation from a large bulk of ethyl acetate.

0·3721 gave 0·6264 CO_2 and 0·1194 H_2O. C = 45·8; H = 3·5.
$C_6H_6O_5$ requires C = 45·6; H = 3·8 per cent.

The basicity of the acid was determined by titration with *N*/10 caustic soda, with phenolphthalein as indicator; the end point is difficult to determine precisely, owing to the deep colour of the resulting sodium salt. The numbers obtained as the equivalent varied from 82—85, that required for a dibasic acid, $C_6H_6O_5$, being 79.

γ-Oxalocrotonic acid is sparingly soluble in water and organic media in general, and is nearly insoluble in benzene, chloroform, or petroleum; it is most abundantly dissolved by acetic or formic acid or methyl or ethyl alcohol, none of which, however, deposits the substance in a well crystallised form. As usually obtained from aqueous or alcoholic solutions, it forms a bright yellow, microcrystalline mass, and it is not easy to ascertain whether it is a uniform substance or a mixture of tautomeric forms, but the author inclines towards the latter view. It melts and decomposes at about 190°.

The cold aqueous solution of the acid is coloured intensely brownish-black by a solution of ferric chloride, indicating the presence of an *enolic* form, whilst on addition of hydrazine acetate immediate yellow precipitates are obtained, indicating that a ketonic form may be present. Hydroxylamine and semicarbazide, however, do not afford sparingly soluble derivatives; with a solution of the former, the yellow colour of the solution becomes much less intense.

Coumalin-6-carboxylic Acid (*α-Pyrone-α'-carboxylic Acid*),

$$CH\begin{matrix}<\\ \\ \end{matrix}\begin{matrix}CH\text{———}CO\\ CH{:}C(CO_2Et)\end{matrix}\begin{matrix}>\\ \\ \end{matrix}O.$$

When diethyl oxalocrotonate is heated with acids, or when the free acid is heated at its melting point, ring formation ensues and a coumalin-carboxylic acid is formed. The most advantageous mode of preparation consists in boiling the ester with excess of fuming hydrochloric acid until complete dissolution has taken place, the liquid being then heated with animal charcoal, filtered, and evaporated to dryness on the water-bath. For further purification, the residue is triturated with enough strong hydrochloric acid to form a paste, transferred to porous earthenware to drain, and then recrystallised two or three times from dilute acetic acid. On analysis:

0·2337 gave 0·4410 CO_2 and 0·0592 H_2O. C = 51·5; H = 2·8.

$C_6H_4O_4$ requires C = 51·43; H = 2·8 per cent.

The equivalent of the acid as determined by titration with caustic soda was 140, or exactly that required for a monobasic acid having the formula $C_6H_4O_4$.

The acid dissolves somewhat sparingly in hot water, alcohol, acetic acid, acetone, or ethyl acetate, and was practically insoluble in benzene, chloroform, or light petroleum. It crystallises best from hot, strong hydrochloric acid. When heated, it melts and decomposes slightly at 227—228°. The crystals from hydrochloric acid are rectangular, transparent plates, or long, transversely striated needles which show a tendency to become twinned. Heated beneath slips of glass, it sublimes slightly before melting, and on cooling solidifies rapidly, forming for the most part a microscopic mass of indistinct structure, but here and there, especially among the sublimed parts, large, well-formed crystals may be seen; in these crystals, the extinction in polarised light is straight, and the directions of greatest elasticity and length are at right angles. On slow sublimation, as during its analysis by the combustion method, it sublimes in brilliant needles.

A dilute solution of the sodium salt gave no precipitates with salts of barium or calcium. A nearly white precipitate was produced on addition of lead acetate, and this dissolved readily in acetic acid; with ferric chloride, a copious, flocculent, brown precipitate was formed, and with mercuric chloride a small quantity of an insoluble salt was precipitated. A cold aqueous or alcoholic solution of the acid gave no coloration with ferric chloride.

On warming the aqueous solution of the acid with silver nitrate and a drop of ammonia, rapid blackening ensues and a brilliant mirror is formed on the walls of the tube. This is doubtless due to the

hydrolysis of the acid to oxalocrotonic acid, as the solution of the acid, when made alkaline with ammonia, warmed, and afterwards acidified gives a very distinct brown coloration with ferric chloride.

When the acid is heated rapidly in a test-tube, a distinct odour of coumalin becomes noticeable, and this substance appears to be formed in small quantity when the calcium salt of the acid is heated strongly in a stream of hydrogen. The aqueous distillate in the latter case, on addition of ammonium sulphate, becomes milky, and a small quantity of a nearly colourless oil is deposited. This, after extraction with ether, had the properties of coumalin so far as the small quantity obtained would permit them to be observed. Thus, it gave a bluish-red coloration with ferric chloride, and evolved an odour resembling that of crotonaldehyde when warmed with alkalis. It may be observed that the odour and colorations were directly compared with those afforded by coumalin made from malic acid in accordance with the directions given by Pechmann (*Annalen*, 1891, **264**, 305), and no difference could be detected.

The acid shows little or no tendency to yield a pyridone derivative when treated with ammonia, but when its ammonium salt is strongly heated with lime, or even alone, a powerful odour of pyridine is evolved, and the distillate affords a perbromide closely resembling that of this base; the large quantity of ammonia and the small quantity of the basic substance in the distillate have hitherto prevented the isolation of any pure pyridine derivative.

Ethyl Coumalin-6-carboxylate, $CH\begin{matrix}CH\text{———}CO\\ CH{:}C(CO_2Et)\end{matrix}O$.—This ester is most easily obtained by the method used by Pechmann in preparing the ester of the isomeric acid, as the properties of the acids and their esters are very similar (*loc. cit.*, 279). It is purified by crystallisation from light petroleum.

0·3808 gave 0·7948 CO_2 and 0·1672 H_2O. C = 56·8; H = 4·9.
$C_8H_8O_4$ requires C = 57·1; H = 4·8 per cent.

The ester is readily soluble in water and in most organic media with the exception of light petroleum, in which it dissolves only sparingly when cold. It crystallises from hot light petroleum in beautiful, thin, rectangular plates melting at 59—60°. The crystals, in polarised light, show interference colours of high orders, and have straight extinction, their directions of greatest length and elasticity being at right angles. After melting, the substance solidifies to opaque masses of long, flattened needles or thin plates.

When covered with 15 per cent. aqueous ammonia, the substance first dissolves, and on stirring, a mass of beautiful, white crystals separates. These disappear on warming, however, and on treatment

with potash, yield a yellow solution which gives the tests for the salt of oxalocrotonic acid; the ester, therefore, is not the ethyl pyridone-carboxylate which it was hoped would be produced. No other method of treatment tried gave any basic substance whatever.

Action of Amyl Formate and Nitrite on Ethyl Crotonate.

Amyl formate and nitrite both react with ethyl crotonate in presence of sodium ethoxide or metallic sodium suspended in dry ether, yielding acidic products in considerable quantity. These are possibly the γ-substituted derivatives sought for, but no attempts to obtain them in a pure form have as yet been successful, nor has any better result been achieved by endeavouring to isolate the corresponding acids. The *iso*nitroso-compound is converted into a basic substance on reduction with sodium amalgam, and it is hoped that by means of this product the nature of the original reaction may be finally ascertained.

Action of Ethyl Oxalate on Ethyl α-Methylacrylate.

Ethyl α-methylacrylate was made by heating ethyl α-bromo*iso*-butyrate with diethylaniline, as recommended by Howles, Thorpe, and Udall (Trans., 1900, 77, 947), but was isolated by distilling the resulting mixture and fractionating the portion which passed over below 160°, a method which appears to afford a somewhat better yield than that recommended by these authors.

The ester was treated with ethyl oxalate in presence of sodium ethoxide and also of sodium and ether, and even under the conditions most advantageous for the formation of ethyl oxalocrotonate, no corresponding oxalyl derivative was obtained, even in an impure condition. This was shown by the fact that, after shaking out the product with water and acidifying the aqueous extract with acetic or hydrochloric acid, no precipitate was produced, and no black coloration was developed on addition of ferric chloride.

It is thus established with some degree of certainty that the formation of ethyl oxalocrotonate is not to be accounted for by the proximity of the negative double binding $CH_3 \cdot \dot{C} : \dot{C}$, for this is also present in ethyl α-methylacrylate. Negative results were also obtained on endeavouring to condense ethyl oxalate with ethyl camphorenate, which contains the grouping $CH_2 \cdot CH : CH$.

Application of the Claisen Reaction to other Compounds containing the Grouping $CH_2 \cdot \dot{C} : \dot{C} \cdot CO$.

On treating ethyl dimethylacrylate, $CMe_2 : CH \cdot CO_2Et$, with ethyl oxalate in presence of sodium and ether or of sodium ethoxide, the bright yellow colour which is characteristic of the early stages in the preparation of ethyl oxalocrotonate at once appears, and if, after a few seconds, the mass is treated with water and the aqueous extract acidified, a colourless oil separates in small quantity, and, on adding ferric chloride to a solution of this in ether, an intense black coloration ensues. If, however, the treatment with sodium or with sodium ethoxide is allowed to continue, the liquid becomes green, and, on adding water, a dark-red, aqueous solution is obtained, which deposits a comparatively small amount of an oil on addition of acetic acid. In both cases, a small quantity of a brown copper compound, resembling that obtained from ethyl oxalocrotonate, may be obtained, but no crystalline substance is produced on decomposing this.

Phorone, $CMe_2 : CH \cdot CO \cdot CH : CMe_2$, reacts very readily with ethyl oxalate in presence of sodium ethoxide, and a large yield of an oily or resinous product is obtained. This affords a black coloration with ferric chloride, and gives a brown, copper salt; it does not yield oxalic acid on alkaline hydrolysis, but gives a sparingly soluble, pulverulent acid which forms an orange-red solution in alkalis.

Benzylidenemesityl oxide, $CMe_2 : CH \cdot CO \cdot CH : CHPh$, also reacts, although somewhat less readily, with ethyl oxalate under the conditions described, and a similar compound is produced. This, as well as the preceding ketone, also reacts with amyl formate or nitrite, but the products are equally uninviting.

Camphorone gives exactly similar derivatives.

Although the products have not yet been obtained in a pure form, it appears probable from these results that there is a line of demarcation between those esters and ketones which contain the grouping

$$\cdot CH_2 \cdot \dot{C} : \dot{C} \cdot CO \cdot$$

and those which do not. The difficulty of obtaining pure substances is due, in part, to the fact that the products are readily decomposed by distillation, even in a vacuum, and also, doubtless, to the readiness with which the $\alpha\beta$-unsaturated esters and ketones undergo decomposition and polymerisation under the conditions of experiment, as has been shown by Pechmann and others (*Ber.*, 1900, 33, 3329, &c.), so that, unless the condensation with the oxalate is sufficiently rapid the product is likely to be of a very mixed character.

The investigation of the foregoing compounds is being continued,

and it is intended that the behaviour of ethyl tetrolate, ethyl α-ethylcrotonate, &c., towards ethyl oxalate should be examined.

The author desires to express his best thanks to the Research Fund Committee of the Chemical Society for a grant which has largely defrayed the cost of the preceding investigation, and with the help of which it is being continued.

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CXXXV.—*The Constitution of Camphanic Acid and of Bromocamphoric Anhydride.*

By ARTHUR LAPWORTH and WALTER HENRY LENTON.

ONE of the most interesting points in connection with the problem of the constitution of camphor and its derivatives is to be found in the behaviour of ordinary bromocamphoric anhydride on hydrolysis. When that substance is boiled with water, especially in presence of sodium carbonate, the anhydride ring is broken, and the bromine atom is simultaneously removed. The product consists for the most part of the lactonic product, camphanic acid, but a certain amount of an unsaturated monobasic acid, lauronolic acid, is also produced, its mode of formation being represented empirically by the equation,

$$C_8H_{13}Br\begin{matrix}CO\\CO\end{matrix}>O + H_2O = C_8H_{13}\cdot CO_2H + HBr + CO_2.$$

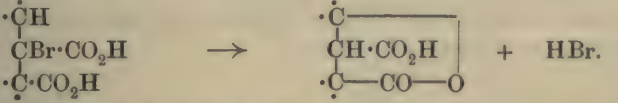
The researches of Fittig and his pupils on brominated acids have brought to light the fact that the removal of carbon dioxide and hydrogen bromide from such compounds by the aid of dilute aqueous alkalis is associated exclusively, or nearly so, in open-chain compounds, with β-bromo-acids, and, generalising from this fact, Aschan (*Ber.*, 1894, **27**, 2114) and others have concluded that in bromocamphoric anhydride the bromine atom must occupy the β-position with regard to one of the two carboxyl groups.

Acceptance of this view, however, is rendered difficult, for the following reasons. Saturated carboxylic acids, on bromination, invariably yield α-bromo-acids. Fittig's observations have reference to the behaviour of β-bromo-acids. Combining these conclusions, we arrive at the view that bromocamphoric acid must be both an α- and a β-bromo-acid, that is to say, it must contain the grouping $CO_2H\cdot\dot{C}Br\cdot\dot{C}\cdot CO_2H$, and be a bromosuccinic acid. Hence it must

follow that camphanic acid belongs to that unstable group of compounds, the β-lactones, of which but few are known, a view which it is almost impossible to reconcile with the great stability of the lactone ring, for hydroxycamphoric acid is unable to exist in the free state, being at once converted into camphanic acid.

Another fact which militates against the probability of the existence of the group $CO_2H\cdot\dot{C}Br\cdot\dot{C}\cdot CO_2H$ in bromocamphoric acid is the fact that lauronolic acid, which, according to this view should contain the grouping $CO_2H\cdot\dot{C}:\dot{C}\cdot$, is not an $\alpha\beta$- but a $\beta\gamma$-unsaturated acid, as is shown by its ready conversion into and formation from campholactone and the corresponding hydroxy-acid.

Other chemists, desiring to maintain that camphoric acid was a derivative of succinic acid, and either ignoring the work of Volhard and others, or attaching less significance to it than to Fittig's observations, have assumed that camphanic acid is a γ-lactonic acid. This assumption necessitates the additional one that camphoric acid either becomes brominated at a point which is not in the α-position with regard to a carboxyl group, or that the bromination follows the usual course, and that the hydrolysis of the bromo-anhydride has involved a change of a type otherwise quite unknown, and representable as follows :



In the hope of being able to prove that the mistake had arisen in generalising too hastily from the behaviour of brominated open chain acids, we have made a long series of experiments with bromocamphoric anhydride and camphanic acid. It was clear from the first that the investigation would be more than usually difficult, for had any straightforward method been available, so important a problem would scarcely have remained for so long a time unsolved.

It was soon found that any views based on the assumption that the change of bromocamphoric anhydride to camphanic acid involved an unusual change of configuration must be set aside, as the reverse change may be effected with great ease by merely warming camphanic acid on the water-bath with phosphorus pentabromide.

The next point to be proved was that camphanic acid was derived from an α-hydroxy-acid. For this purpose, and for a long time without success, we sought a method of removing the carboxyl group which was presumed to be attached to the same carbon atom as the hydroxyl group. The removal of a carboxyl group from an α-hydroxy-acid is, as a rule, a fairly easy process, and in a large number of cases may be achieved by such simple means as heating with strong acids, or with

chromic acid or lead peroxide in presence of dilute acetic acid. In the present case, however, it would appear that the absence of the actual hydroxyl group itself, which is altered by its participating in the formation of the stable lactone ring, renders the usual oxidation processes entirely ineffectual. Attempts were also made to oxidise the product in which the lactone ring is opened (obtained by boiling the acid with excess of alkali); these were more effectual, but as the oxidation went too far, the experiments gave no useful result.

Eventually, however, the nitrile of camphanic acid was prepared in the hope that, like the α-hydroxynitriles, it would prove to be unstable towards alkalis. For this purpose camphanamide was required as an intermediate product and it was obtained by the following methods.

Camphanic acid was heated with phosphorus trichloride and the product poured into ammonia; a small quantity of the amide was thus obtained, but the process was tedious and the yield unsatisfactory. The amide was obtained much more easily, however, by a modification of Wreden's method. Wreden heated bromocamphoric anhydride with ammonia in closed tubes, and obtained a substance which he took to be the imide of hydroxycamphoric acid (*Annalen*, 1872, **163**, 339), but which is identical with the amide made by the above process, behaves neither as a hydroxy-compound nor as an imide, and, as our subsequent work showed, must be regarded as camphanamide. The action is represented by the equation

$$C_8H_{13}Br\begin{matrix}CO\\CO\end{matrix}O + 2NH_3 = NH_4Br + NH_2\cdot CO\cdot C_8H_{13}\begin{matrix}O\\CO\end{matrix}.$$

The heating in sealed tubes was found to be unnecessary, as it was sufficient to leave the finely-powdered bromoanhydride with strong ammonia for several hours at the ordinary temperature in order to effect its almost complete conversion into the amide.

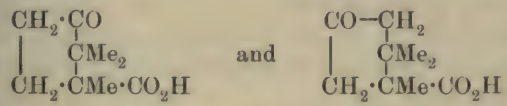
The amide was then converted into the nitrile by heating it with a mixture of phosphorus trichloride and pentachloride. A waxy nitrilolactone was thus produced, which, on treatment with strong alkalis, was resolved into hydrogen cyanide and camphononic acid (Lapworth and Chapman, Trans., 1899, **75**, 1000). As this is a γ-ketonic acid, the investigation has afforded an apparently incontrovertible proof of the views which we hold of the relationship of bromocamphoric acid and camphanic acid to camphoric acid itself.

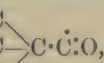
The course of the changes involved may be represented by the scheme,

$$\begin{matrix}CH_2\cdot C\cdot CO\cdot NH_2\\ |\quad\ CMe_2\\ CH_2\cdot CMe\cdot CO\cdot O\end{matrix} \rightarrow H_2O + \begin{matrix}CH_2\cdot C\cdot CN\\ |\quad\ CMe_2\\ CH_2\cdot C\cdot Me\cdot CO\cdot O\end{matrix} \rightarrow HCN + \begin{matrix}CH_2\cdot C{:}O\\ |\quad\ CMe_2\\ CH_2\cdot CMe\cdot CO_2H\end{matrix}$$

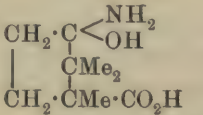
and it may be worth while to point out that a combination of the above facts with those already known about camphononic acid (*loc. cit.*) is in itself sufficient to decide almost conclusively the true constitution of camphoric acid.

Thus, it has been shown that camphononic acid has one or other of the two formulæ,



and of these, in reality, only the former can be deemed worthy of serious consideration, for the acid yields hydrazones, a semicarbazone, and an oxime only with difficulty, does not unite with hydrogen cyanide, and cannot be reduced by such energetic treatment as with sodium and boiling amyl alcohol. Such a behaviour is altogether unknown in simple ketones and ketonic acids which contain the grouping $\cdot CH_2 \cdot CO \cdot CH_2 \cdot$, present in the second of the above formulæ; the properties of such an acid would approach more nearly those of camphonic acid (Trans., 1900, 77, 454), which has a constitution of that kind. The first of the above formulæ, therefore, apart from any views as to the constitution of camphor or camphoric acid, is the only possible one, containing as it does the grouping  , which is characterised by an exceptionally feeble tendency to form additive complexes (compare Trans., 1901, 79, 379).

In extending the foregoing observations, we have succeeded in devising a second method of converting camphoric acid into camphononic acid, through camphanamide as the intermediate stage. In this method, advantage was taken of the fact that the additive compounds of ammonia with aldehydes or ketones are easily broken down under the influence of alkalis or acids. In order to obtain the analogous compound of camphononic acid, the amide of camphanic acid was subjected to the action of sodium hypobromite and excess of sodium hydroxide. It was expected that the $CO \cdot NH_2$ group would, as usual, be converted into the NH_2 group, and that an unstable aminohydroxy-acid of the formula



would be produced which would at once break down into ammonia and camphononic acid. As a matter of fact, by this process, large quan-

tities of the ketonic acid may be prepared, and in a shorter time than by any of the methods hitherto discovered.

Experimental.

The camphanic acid used in these experiments was prepared from bromocamphoric anhydride by boiling it with potassium acetate dissolved in glacial acetic acid, and removing the potassium bromide from time to time by filtration, in accordance with Aschan's directions (*Acta soc. scient. fenn.*, 21, No. 5, 1).

Dry camphanic acid is best made by heating the hydrated crystals in a flask at 200°, a stream of air being occasionally drawn through the flask to remove the steam. On cooling, it is noticed that the whole sets to a semi-transparent mass of crystals, and that this afterwards becomes opaque; this change is due to dimorphism, and is most easily observed in the following way.

The camphanic acid is melted on a microscope slide beneath a cover glass; on cooling, the substance sets rapidly to a transparent isotropic mass the structure of which is difficult to distinguish, but consists of a conglomeration of crystals resembling ammonium chloride; almost immediately afterwards, the appearance of the second, doubly refracting, ordinary modification is noticed, the field now becoming distinctly crystalline.

Camphanic acid is very stable towards most, and especially towards acid, oxidising agents. Thus, when heated with lead peroxide and acetic acid, it does not afford any appreciable quantity of carbon dioxide. It is very slowly attacked by nitric acid, however, and is practically converted into camphoronic acid, the intermediate compounds, if any, being less stable towards the agent than camphanic acid itself.

Attempts were made to obtain a ketonic acid by boiling the camphanic acid with excess of potash to hydrolyse the lactone ring, and the resulting solution of the potassium hydroxycamphorate was diluted and partially neutralised by means of a stream of carbon dioxide. A 2 per cent. solution of potassium permanganate was then run in, and as it was found that decolorisation occurred only very slowly, excess of the oxidising solution was added, and the whole allowed to remain for several days at 0°; the solution was then decolorised by means of sulphurous acid, heated, filtered, and evaporated. On acidifying and extracting the residue with ether, an oily mixture was obtained, which soon deposited a considerable quantity of crystals of unaltered camphanic acid; the remaining portion gave a very small deposit when warmed with a solution of phenylhydrazine acetate, but the amount of this was insufficient to be of any value for further investigation.

Experiments were then tried with campholactonic acid, which is usually supposed to be closely related to camphanic acid, as it was possible that it might be the hydroxy-acid corresponding with camphononic acid. It was made by hydrolysing purified campholactone, and formed beautiful, white crystals melting at 146°. The purified acid was dissolved in sodium carbonate solution, cooled to 0° and treated in the usual manner with dilute potassium permanganate, which at first was instantly decolorised, but when a comparatively small quantity had been added, retained its colour for a long time. The products, isolated in the usual way, contained substances of a ketonic character, but the insoluble phenylhydrazones obtained from it, curiously enough, were insoluble in dilute sodium carbonate, and were, therefore, not simple hydrazones of ketonic acids. From this it would appear that campholactonic acid is not genetically related to camphononic acid in the simple manner commonly supposed.*

Preparation of Camphanamide, $NH_2 \cdot CO \cdot C_8H_{13} < \begin{matrix} O \\ | \\ CO \end{matrix}$.

In attempting to obtain camphanamide, the first experiments were made with the object of preparing it from the chloride of camphanic acid. For this purpose, the dry, finely powdered acid was heated in a flask with a large excess of phosphorus trichloride for several hours, the excess of the latter boiled off, the residue dissolved in ether to render it more easy to manipulate, and the ethereal solution gradually poured into strong aqueous ammonia, which was kept at 0° and shaken continuously. A small quantity of a white, pulverulent substance separated, which was collected by filtration, washed, and crystallised from methyl alcohol, when it separated in brilliant prisms melting at 160°.

When warmed with dilute soda, the substance slowly dissolved, and on acidifying the resulting solution, a sparingly soluble acid separated. This melted at 160°, with evolution of water vapour, solidified immediately, and afterwards melted at the same temperature as the original amide.

The properties of the two foregoing substances resembled very

* The author has suggested the formula $\begin{matrix} CH_2 \cdot CMe \\ | \quad \| \\ | \quad CMe \\ | \quad | \\ CH_2 \cdot CMe \cdot CO_2H \end{matrix}$ as a probable one for lauronolic acid (*Brit. Assoc. Report*, 1900, 327). If this is correct, then the formula for the corresponding γ-hydroxy-acid, namely, campholactonic acid, would be $\begin{matrix} CH_2 \cdot CMe — O \\ | \quad | \\ | \quad CHMe \quad | \\ | \quad | \\ CH_2 \cdot CMe — CO \end{matrix}$.

closely those of the compound obtained by Wreden from bromocamphoric anhydride by heating it with ammonia in closed tubes (*loc. cit.*), and it was thought, therefore, that a better yield might be obtained by his process. On repeating his experiments, it was found that the compounds were, in fact, identical, and, moreover, that it was unnecessary to employ heat during the process, as, when the bromoanhydride was sufficiently finely powdered, a marked development of heat occurred spontaneously on adding it to ammonia. We have, therefore, used the following process in preparing the amide.

The anhydride is powdered as finely as possible, passed through a fine sieve, and projected, in small quantities at a time, into a flask containing strong aqueous ammonia (sp. gr. 0·880), which is agitated during the whole time to prevent the formation of lumps. In the course of 24 hours, the powder is converted into a mass of minute needles, which may be collected at the pump, washed, and crystallised from methyl alcohol or acetone. On analysis:

0·1947 gave 0·4377 CO_2 and 0·1371 H_2O. C = 60·8; H = 7·8.
0·2390 „ 13·9 c.c. moist nitrogen at 13° and 750 mm. N = 6·8.
$C_{10}H_{15}O_3N$ requires C = 60·9; H = 7·6; N = 7·1 per cent.

Camphanamide has all the properties ascribed to it by Wreden (*loc. cit.*). It dissolves sparingly in water, cold alcohol, or ethyl acetate, more readily in hot methyl or ethyl alcohol or acetone, and separates from the last-named solvent in beautiful, transparent prisms of calcite-like lustre.

The crystals are apparently of rhombic symmetry; in crushed fragments, in convergent polarised light, a wide biaxial figure is occasionally seen. The melted substance solidifies readily in long needles, flattened in a direction perpendicular to the optic axial plane. The directions of greatest length and elasticity are at right angles to one another.

That the compound is in reality an amide, and not, as Wreden supposed, a hydroxyimide, is shown by the fact that it does not behave like an imide in any way, and gives no silver compound on treatment with ammonia and silver nitrate. Its identity with the substance obtained from the chloride of camphanic acid tells in favour of the view that it is an amide. Further, and perhaps more conclusive, evidence is afforded by the fact that it was not found possible, even with Franchimont's mixture of acetic anhydride and sulphuric acid, to prepare an acetyl derivative, the substance remaining unattacked after treatment for several hours at 130°.

Camphanamic Acid, $NH_2{\cdot}CO{\cdot}C_8H_{13}(OH){\cdot}CO_2H$.—This compound is easily prepared by warming powdered camphanamide with 10 per cent. sodium hydroxide solution, and, after precipitation with hydrochloric

acid, may be crystallised from dilute alcohol. A specimen was analysed, after exposure at 100° for 9 hours.

0·2172 gave 0·4529 CO_2 and 0·1613 H_2O. C = 56·8 ; H = 8·2.
$C_{10}H_{17}O_4N$ requires C = 56·0 ; H = 7·9 per cent.

The substance, when crystallised from dilute alcohol, contains 1 mol. of water of crystallisation. It dissolves somewhat readily in alcohol, is sparingly soluble in ethyl acetate, and insoluble, or nearly so, in benzene or light petroleum. From a mixture of methyl alcohol and ethyl acetate, it separates in beautiful, transparent prisms of considerable size, which have a brilliant lustre, a well-marked plane of cleavage, and readily break up into thin plates. The double refraction is weak.

The melting point of the substance is difficult to determine with any certainty, owing to the difficulty of getting rid of the water of crystallisation and the readiness with which the acid is converted into the lactone. When slowly heated, it melts at 160°, as stated by Wreden, but when the tube containing it is plunged into sulphuric acid at 155°, fusion does not occur until a temperature of 165—166° is reached. In all cases, an effervescence, due to the escape of water-vapour, accompanies the fusion, and the residue soon solidifies, the mass melting once more at 208°, the melting point of camphanamide.

A dilute solution of the ammonium salt gives no precipitate with solutions of calcium or barium salts ; a white precipitate is produced with warm basic lead acetate, and with ferric chloride a nearly white precipitate is formed, which, on warming, disappears, the whole becoming reddish-brown.

Action of Dehydrating Agents on Camphanamide.

Camphanonitrile, $CN\cdot C_8H_{13}<\overset{O}{\underset{CO}{|}}$.

Camphanamide is not easily converted into the corresponding nitrile ; zinc chloride, phosphoric oxide, or phosphoric sulphide either produced no effect on it or converted it into a charred mass. By the following process, however, a small quantity of the desired product may be obtained.

The finely powdered amide is placed in a flask, uncovered, with a large excess of phosphorus trichloride, one molecular proportion of phosphorus pentachloride is added, and the whole heated on the water-bath until the particles of the amide are no longer distinguishable. The flask is then cooled, and the contents are poured slowly on to powdered ice which is kept well stirred. Chloroform is then added, the whole well shaken, and the chloroform extract shaken repeatedly with very dilute sodium carbonate solution, dried with calcium

chloride, and evaporated to dryness. The green or greenish-black, oily residue is extracted repeatedly with large quantities of light petroleum, and the waxy material which separates from the hot solutions crystallised several times from the same solvent, until it melts at 135°. A specimen dried in a vacuum was analysed:

0·2345 gave 0·5777 CO_2 and 0·1506 H_2O. C = 67·2; H = 7·1.
$C_{10}H_{13}O_2N$ requires C = 67·0; H = 7·3 per cent.

Camphanonitrile forms soft, fern-like crystals resembling those of ammonium chloride, which aggregate on pressure to a waxy, camphor-like mass. Melted on a slip of glass, it solidifies rapidly and completely, forming skeleton crystals whose branches are rectangularly arranged, the whole being completely isotropic. The highest melting point observed for the substance was 135—137°, but was never quite sharp, and it is possible that this temperature is a few degrees too low. When heated slowly at a higher temperature, the substance distils, apparently without much decomposition, and the vapour has an odour resembling that of raspberries.

The nitrile dissolves in about five times its weight of sulphuric acid without decomposition, and if the solution is mixed with an equal bulk of fuming acid (25 per cent. SO_3) and the mixture poured into ice, a small quantity of nearly pure camphanamide is obtained, showing that no structural change has been involved in the action of dehydrating agents on the amide.

Action of Alkalis on Camphanonitrile. Formation of Camphononic Acid.

When camphanonitrile is covered with 20 per cent. aqueous potassium hydroxide, no immediate effect is observed, but if the whole is warmed or allowed to stand for some time the solid slowly disappears and a clear solution is finally obtained. On acidifying this solution, effervescence occurs and a strong odour of hydrogen cyanide becomes perceptible, the actual presence of this substance being easily shown by the usual tests.

When the strongly acidified solution is extracted with chloroform in the usual way, a transparent, waxy mass remains on evaporating the extract. This substance crystallises from ethyl bromide in small prisms melting at 228° and has all the properties of camphononic acid. On analysis:

0·3713 gave 0·8583 CO_2 and 0·2760. C = 63·1; H = 8·1.
$C_9H_{14}O_3$ requires C = 63·5; H = 8·2 per cent.

In order to obtain further proof of the identity of the acid, it was converted into the oxime. This crystallised from methyl alcohol in

large, transparent rhombohedra which rapidly became opaque on exposure to the air, and as the substance melted at 186—187° the identity of the acid with camphononic acid was certain.

Action of Sodium Hypobromite and Sodium Hydroxide on Camphanamic Acid.

Eighteen grams of the amide were dissolved in 100 c.c. of 10 per cent. sodium hydroxide solution by the aid of warmth; to the resulting liquid 13 c.c. of bromine dissolved in 350 c.c. of sodium hydroxide were added, and the whole was heated on the water-bath for an hour. The excess of hypobromite was removed by means of sodium sulphite, and the liquid then acidified and evaporated to dryness, any unaltered amide which separated during this process being removed from time to time. The residue was then extracted with dehydrated methylated spirit, and the extracted matter shaken with chloroform several times, the extract being evaporated to dryness. A waxy or oily residue remained, which was first triturated with ethyl bromide and afterwards crystallised from the same solvent.

The substance thus obtained consisted almost entirely of pure camphononic acid, as was proved by the methods just described. By the treatment of 55 grams of camphanamide in this way, the recovered amide being repeatedly subjected to the same process, a quantity of pure camphononic acid weighing 17 grams was finally obtained, and the process occupied only a few days.

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CXXXVI.—*The Chlorodibromo- and Dichlorobromo-benzenes.*

By William Holdsworth Hurtley, D.Sc. (Lond.).

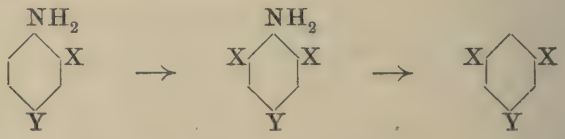
According to theory, there should be twelve trisubstituted benzenes containing either one atom of chlorine and two atoms of bromine, or two of chlorine and one of bromine. Six of these are unsymmetrical in structure, two symmetrical, and four vicinal. Of these twelve, the two symmetrical compounds have been obtained by Hantzsch, Schleissing, and Jäger (*Ber.*, 1897, 30, 2334); the *s*-chlorodibromobenzene by the transformation of the acid *s*-tribromobenzenediazonium chloride; and the *s*-dichlorobromobenzene by the transformation of the same compound on standing and warming. The *s*-chlorodibromo-

benzene was also obtained by them from 3 : 5-dibromoaniline, by replacing the amino-group by chlorine.

In this paper, the preparation of all the twelve chlorobromobenzenes from anilines of known constitution is described. The unsymmetrical compounds were all obtained by replacing the amino-group in di-halogen amines by chlorine or bromine, and, for this purpose, Gattermann's well-known method (*Ber.*, 1890, **23**, 1222) was employed. Several of the unsymmetrical compounds were also obtained by replacing the amino-group in tri-halogen anilines by hydrogen.

The symmetrical and vicinal compounds were prepared by replacing the amino-group in the corresponding chlorobromoanilines by hydrogen, by the method first described by Griess (*Annalen*, 1866, **137**, 67). Any unsymmetrical tri-halogen benzene can be prepared from acetanilide by introducing two halogen atoms, when a compound of the formula 

results, where X, and also Y, may be either chlorine or bromine. On hydrolysing the acetyl derivative and replacing the amino-group by chlorine or bromine, the desired compound is obtained. Further treatment with a halogen converts the 2 : 4-halogen anilines into the symmetrical tri-halogen compounds, from which the symmetrical chlorodibromo- or dichlorobromo-benzenes are obtained by removing the amino-group. Thus:



where X, and also Y, may be either chlorine or bromine.

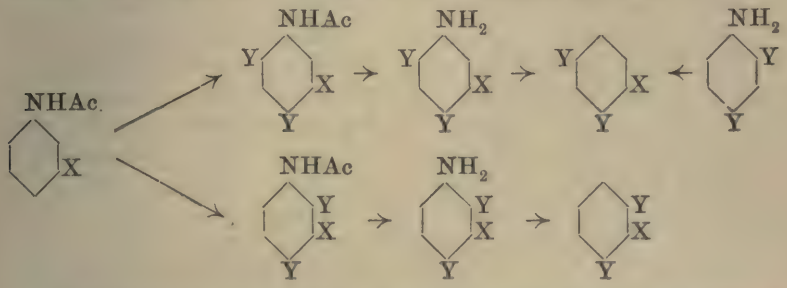
Two, and only two, tri-halogen anilides are obtained when a meta-halogen anilide is treated with chlorine or bromine. One of these has a higher melting point, is less soluble in alcohol, 50 per cent. acetic acid, or benzene, and is formed in much larger amount than the other. The substance of higher melting point has the halogens in the positions 2 : 4 : 5; this is proved:

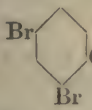
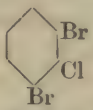
(*a*) By hydrolysing the acetyl derivative and removing the amino-group, when an unsymmetrical tri-halogen benzene results.

(*b*) By the fact that the same anilide is obtained as principal product on introducing one halogen atom into the 3 : 4-halogen anilide.

The other anilide may have the halogen atoms in the positions 2 : 3 : 4, 3 : 4 : 5, or 2 : 3 : 6. It is produced together with a larger amount of the isomeric 2 : 4 : 5-compound when one halogen atom enters

into the 3 : 4-di-halogen anilide, and, on removing the amino-group, does not yield an unsymmetrical tri-halogen benzene. Hence it is not a 2 : 3 : 6-derivative. It is not a dimeta-derivative, because, apart from the improbability of the formation of such a compound, I have shown that on brominating *m*-dichloroacetanilide the product is not identical with that which results on chlorinating *m*-bromoacetanilide, although both yield the same dichlorobromobenzene. The anilide having the lower melting point must therefore be a 2 : 3 : 4-derivative. Thus we have :



If this scheme is correct, we should obtain as final products the compounds  and  , on brominating *m*-chloroacetanilide; the first compound should be identical with that prepared by replacing the amino-group in 2 : 4-dibromoaniline by chlorine, and the second with that formed on replacing the amino-group in 2 : 6-dibromoaniline by chlorine. This has been shown to be the case.

The quantities of the tri-halogen benzenes at disposal for the determination of chemical and physical properties were about 3 grams each in the case of vicinal derivatives, and about 10 grams in each of the others. The vicinal compounds crystallise in well-defined, rhombic plates, the symmetrical in long, slender prisms, and the unsymmetrical in short, thin prisms.

The chlorodibromo- and dichlorobromo-benzenes are very soluble in benzene, ether, chloroform, or petroleum, but less so in alcohol, from which they can all be readily crystallised. The unsymmetrical compounds are very slowly volatile in steam, in which, however, the symmetrical and vicinal derivatives volatilise readily. The vicinal and unsymmetrical compounds have a characteristic bromobenzene-like odour, whilst the symmetrical derivatives have a very faintly mouldy one.

The melting and boiling points of these tri-halogen benzenes show interesting regularities; these constants, with those of the trichloro- and tribromo-benzenes, are collected in the following table :

Trichlorobenzenes.

	M. p.	B. p.
1:2:4	16°	213°
1:2:3	53	218
1:3:5	63	208

Tribromobenzenes.

	M. p.	B. p.
1:2:4	44°	275°
1:2:3	87	—
1:3:5	120	271

Dichlorobromobenzenes.

	Cl:Cl:Br	M. p.	B. p.
as	1:2:4	24·5°	237°
	1:3:4	25	235
	1:4:2	33	235
v	1:2:3	60	243
	1:3:2	65	242
s	1:3:5	77·5	232

Chorodibromobenzenes.

	Cl:Br:Br.	M. p.	B. p.
	1:3:4	36°	256°
	1:2:4	27	258
	1:2:5	40·5	259
	1:2:3	73·5	264
	1:2:6	69·5	265
	1:3:5	99·5	256

A consideration of this table shows that the melting point depends on both the nature and position of the substituents, whilst the boiling point depends more on the former than on the latter. Thus, the melting point of 1 : 3-dichloro-2-bromobenzene is 32° higher than that of 1 : 4-dichloro-2-bromobenzene, whilst the boiling points differ only by 7°; the melting point of 1-chloro-2 : 3-dibromobenzene is 33° higher than that of 1-chloro-2 : 5-dibromobenzene, whilst the boiling points differ only by 5°; the melting points of the symmetrical compounds are much higher, but their boiling points are slightly lower, than those of the unsymmetrical derivatives. The symmetrical compounds have the highest melting point, the vicinal are intermediate, and the unsymmetrical have the lowest melting point; this is also true for the trichloro- and tribromo-benzenes.

In the case of the boiling points, the vicinal compounds boil at the highest temperature, the unsymmetrical are intermediate, and the symmetrical compounds have the lowest boiling points. This order applies to the trichlorobenzenes and also to the trimethylbenzenes. The boiling point of the vicinal tribromobenzene is not given in Beilstein's *Handbuch*, and those of the unsymmetrical and symmetrical compounds are given as 275° and 278° respectively. As the symmetrical tribromobenzene would be expected to conform to the same rule as the other compounds, and boil at a lower temperature than the unsymmetrical derivative, I made a specimen of this substance by removing the amino-group from symmetrical tribromoaniline, and purified the product by crystallisation from alcohol and distillation in a vacuum; it boiled at 271° under 765 mm. pressure, thus conforming to the rule.

Experimental.

1 : 2-*Dichloro-4-bromobenzene.*

This compound was prepared from 2-chloro-4-bromoacetanilide, which was obtained from *p*-bromoacetanilide by the method described by Chattaway and Orton (this vol., p. 820).

The base from the 2-chloro-4-bromoacetanilide was dissolved in a large excess of concentrated hydrochloric acid (ten times the calculated quantity), some water added, diazotised at 0° with sodium nitrite, and the solution of the diazochloride added to freshly made, well washed, precipitated copper. This product was extracted with chloroform, filtered, the chloroform removed by distillation, and the residue distilled in a vacuum. From the non-volatile portion, by washing with ether, a substance having all the properties of an azo-derivative was isolated; it is being examined. The 1 : 2-dichloro-4-bromobenzene was again distilled in a vacuum, when it boiled constantly at 124° under 33 mm. pressure, with the oil-bath at 134°. When crystallised from alcohol, it formed short prisms melting at 24·5°. It boiled at 237° under 757 mm. pressure. This and all the other boiling points under atmospheric pressure, described in this paper, were determined by Siwoloboff's method (*Ber.*, 1886, 19, 795).

0·1787 gave 0·3757 AgCl + AgBr and 0·2553 Ag. Cl = 30·63; Br = 36·74.

$C_6H_3Cl_2Br$ requires Cl = 31·38; Br = 35·40 per cent.*

1 : 3-*Dichloro-4-bromobenzene.*

The amino-group in 2 : 4-dichloroaniline was replaced by bromine exactly as above described, except that hydrobromic acid was used in place of hydrochloric acid. Gattermann states that a mixture of sulphuric acid and potassium bromide can be added to the diazochloride in place of hydrobromic acid, but in this preparation a better yield resulted when the latter was used. On distilling the copper mixture in a current of steam, it was found that the product came over very slowly, and, subsequently, extraction with chloroform was used instead of this process. On distillation in a vacuum, the dichlorobromobenzene boiled at 111° under 21 mm. pressure, with the oil-bath at 130°. It crystallised in clusters of small, white prisms which melted at 25° and boiled at 235° under 751 mm. pressure.

* The mixed silver salts were weighed in a small Gooch crucible; this was then placed in a small Rose crucible and heated in a stream of dry hydrogen. In the above analysis, the mixed chloride and bromide was only 0·0002 too high and the silver 0·0008 too low; as these errors are in opposite directions they make the found percentages of chlorine and bromine show considerable divergence from the calculated values. This occurs in two or three cases in the present paper.

0·1586 gave 0·3350 AgCl + AgBr and 0·2291 Ag. Cl = 32·05; Br = 34·71.
$C_6H_3Cl_2Br$ requires Cl = 31·38; Br = 35·40 per cent.

This compound was also prepared by removing the amino-group from 2 : 4-dichloro-5-bromoaniline (p. 1302).

1 : 4-*Dichloro*-2-*bromobenzene.*

2-Bromo-4-chloroaniline was employed for the preparation of this compound. *p*-Chloroacetanilide was dissolved in glacial acetic acid, and to the solution one molecular proportion of bromine dissolved in acetic acid was added, along with some fused sodium acetate. The product so obtained was precipitated by water, crystallised from alcohol, and hydrolysed, and the amino-group of the resulting aniline replaced by chlorine. After extraction with chloroform and removal of the latter by distillation, the residue was distilled in a vacuum. From the non-volatile portion an azo-compound was isolated by washing with ether. The distillate was redistilled, and came over at 119° under 26 mm. pressure, with the bath at 141°. 1 : 4-Dichloro-2-bromobenzene crystallised from alcohol in short prisms, melted at 33°, and boiled at 235° under 751 mm. pressure.

0·2812 gave 0·5898 AgCl + AgBr and 0·4014 Ag. Cl = 30·87; Br = 36·13.
$C_6H_3Cl_2Br$ requires Cl = 31·39; Br = 35·40 per cent.

This compound was also obtained by removing the amino-group from 3 : 6-dichloro-4-bromoaniline (p. 1301).

1-*Chloro*-3 : 4-*dibromobenzene.*

On replacing the amino-group in 2-bromo-4-chloroaniline by bromine, only a very poor yield of this compound was obtained. Accordingly, another method of preparation was used: 3 : 4-dibromoacetanilide was prepared by dissolving *m*-bromoacetanilide in glacial acetic acid, and adding the calculated amount of bromine, also dissolved in glacial acetic acid. After precipitation by water, and crystallisation from alcohol, a pure product was obtained (compare Körner, *Gazzetta*, 1874, 4, 330). This was hydrolysed, and the amino-group replaced by chlorine, the rest of the process being exactly similar to that already described. Under 19 mm. pressure, the new compound distilled at 121°, with the bath at 141°. As the distillate was slightly green, it was distilled in steam, and three times crystallised from alcohol. 1-Chloro-3 : 4-dibromobenzene crystallised in short prisms, which melted at 35·5°, and boiled at 256° under 760 mm. pressure.

0·2232 gave 0·4285 AgCl + AgBr and 0·2665 Ag. Cl = 12·68; Br = 59·83.
$C_6H_3ClBr_2$ requires Cl = 13·11; Br = 59·14 per cent.

This compound was also obtained by replacing the amino-group in 2-chloro-4 : 5-dibromoaniline by hydrogen (p. 1305).

1-*Chloro*-2 : 4-*dibromobenzene*.

The amino-group in 2 : 4-dibromoaniline is easily replaced by chlorine, and the new compound is obtained in a pure condition in exactly the same way as the preceding substance. Under 41 mm. pressure, and with the bath at 152°, it boils at 139°; its melting point is 27°, and it boils at 258° under 757 mm. pressure.

0·1878 gave 0·3593 AgCl + AgBr and 0·2240 Ag. Cl = 13·04; Br = 59·04.
$C_6H_3ClBr_2$ requires Cl = 13·11; Br = 59·14 per cent.

This compound was also obtained by eliminating the amino-group from 3-chloro-4 : 6-dibromoaniline (p. 1304).

1-*Chloro*-2 : 5-*dibromobenzene*.

p-Dibromobenzene was prepared by brominating benzene in presence of iodine (Jannasch, *Ber.*, 1877, 10, 1355), and nitrated by careful addition of fuming nitric acid, the mixture being kept cool during the process. The *p*-dibromonitrobenzene was reduced by tin and hydrochloric acid, the amino-group in the resulting aniline replaced by chlorine, and the 1-chloro-2 : 5-dibromobenzene purified as above. It distils at 121° under 24 mm. pressure, with the bath at 150°.

Another method employed for its preparation was as follows. 3-Bromo-4-chloroacetanilide was prepared from *m*-bromoacetanilide by transformation of the nitrogen chloride of the latter, and separated from the 3-bromo-6-chloroacetanilide formed at the same time by hydrolysing the mixed anilides with alcohol and sulphuric acid and distilling the product in steam, when 3-bromo-4-chloroaniline remained behind as sulphate. This salt was decomposed, and the aniline purified by distillation in steam and crystallisation from chloroform. After acetylation, the resulting anilide was brominated, yielding 2 : 5-dibromo-4-chloroacetanilide which, on hydrolysis and removal of the amino-group, gave 1-chloro-2 : 5-dibromobenzene.

This chlorodibromo-derivative melts at 40·5° and boils at 259° under 764 mm. pressure.

0·1701 gave 0·3299 AgCl + AgBr and 0·2065 Ag. Cl = 13·85; Br = 58·69
$C_6H_3ClBr_2$ requires Cl = 13·11; Br = 59·14 per cent.

1 : 3-*Dichloro*-5-*bromobenzene.*

2 : 4-Dichloro-6-bromoaniline was prepared by adding a glacial acetic acid solution of the calculated amount of bromine to a solution of 2 : 4-dichloroaniline in the same solvent, in presence of fused sodium acetate. The product was precipitated by water and crystallised from alcohol. The amino-group, in this and all other cases referred to in this paper, was removed as follows. The aniline was treated with sulphuric acid of such a strength that it dissolved fairly readily on warming. The solution, cooled to 0°, was saturated with nitrous fumes from arsenious oxide and nitric acid (sp. gr. 1·35), and the resulting green liquid poured into excess of alcohol. On warming, the 1 : 3 dichloro-5-bromobenzene crystallised out and was purified by distillation in steam and two crystallisations from alcohol.

This compound was also obtained by the following method. *p*-Bromoaniline, dissolved in glacial acetic acid, was saturated with chlorine, made alkaline, and distilled in steam. The 2 : 6-dichloro-4-bromoaniline so obtained was crystallised from alcohol and the amino-group removed as just described.

1 : 3-Dichloro-5-bromobenzene crystallises in long, slender prisms having a very faint, mouldy odour, melts at 77·5°, and boils at 232° under 757 mm. pressure. Hantzsch (*loc. cit.*) gives its melting point as 82—84°.

0·1680 gave 0·3538 AgCl + AgBr and 0·2411 Ag. Cl = 31·25 ; Br = 35·83.
$C_6H_3Cl_2Br$ requires Cl = 31·38 ; Br = 35·40 per cent.

1-*Chloro*-3 : 5-*dibromobenzene.*

A glacial acetic acid solution of *p*-chloroaniline was treated with a solution of 2 mols. of bromine in the same solvent, in presence of fused sodium acetate. The resulting 2 : 6-dibromo-4-chloroaniline was precipitated from the solution by water, crystallised from alcohol, and the amino-group removed as already described. To purify the product, it was distilled in steam and crystallised twice from alcohol.

This compound was also prepared in a precisely similar manner from *o*-chloroaniline.

1-Chloro-3 : 5-dibromobenzene closely resembles the symmetrical dichlorobromobenzene. It melts at 99·5° and boils at 256° under 757 mm. pressure. Hantzsch (*loc. cit.*) gives the melting point as 96°.

0·1660 gave 0·3216 AgCl + AgBr and 0·2011 Ag. Cl = 13·63; Br = 58·89.
$C_6H_3ClBr_2$ requires Cl = 13·11 ; Br = 59·14 per cent.

This compound was also prepared from 3 : 5-dibromoaniline (10 grams

of which Dr. Chattaway kindly gave me for this purpose) by replacing the amino-group by chlorine.

1 : 2-*Dichloro*-3-*bromobenzene.*

m-Chloroacetanilide was dissolved in glacial acetic acid and the solution treated in presence of fused sodium acetate with the calculated amount of bromine also dissolved in acetic acid. On precipitating the product by water and crystallising from alcohol, pure 3-chloro-4-bromoacetanilide was obtained. This substance was dissolved in glacial acetic acid and saturated with dry chlorine, when a crystalline solid separated. The solid and the mother liquor were worked up separately as follows.

The solid was principally a mixture of nitrogen chlorides; so it was dissolved in alcohol and a little ammonia added to decompose them. From this solution crystals melting at about 170° separated; they were recrystallised until they melted constantly at 189°. The mother liquor from the crystals, melting at 170°, was precipitated by water and the precipitate crystallised from alcohol, when a product melting at about 135° resulted, which was recrystallised until it melted constantly at 138·5°.

The mother liquor was precipitated by water and the product dissolved in alcohol, some ammonia being added for the reason just given. The crystals thus obtained melted at about 132°; and by repeated crystallisation from alcohol were separated into a small quantity of the anilide melting at 189°, and a second anilide melting constantly at 138·5°.

3 : 6-*Dichloro*-4-*bromoacetanilide* crystallises in thin prisms and is sparingly soluble in alcohol, benzene, or 50 per cent. acetic acid. It melts at 189°.

0·2143 gave 0·3596 AgCl + AgBr and 0·2454 Ag. Cl = 25·13; Br = 28·16.
$C_8H_6ONCl_2Br$ requires Cl = 25·06; Br = 28·26 per cent.

3 : 6-*Dichloro*-4-*bromoaniline*, obtained from the anilide by hydrolysis with alcohol and sulphuric acid, crystallises in needles. It is readily soluble in alcohol, petroleum, or ether, and melts at 91°.

0·2144 gave 0·4218 AgCl + AgBr and 0·2875 Ag. Cl = 29·23; Br = 33·33.
$C_6H_4NCl_2Br$ requires Cl = 29·43; Br = 33·19 per cent.

The constitution of this aniline, and therefore that of the anilide also, was proved by removing the amino-group, when 1 : 4-dichloro-2-bromobenzene was obtained.

2 : 3-*Dichloro*-4-*bromoacetanilide* is far more soluble in alcohol, benzene,

or 50 per cent. acetic acid than the isomeric unsymmetrical anilide. It crystallises in prisms and melts at 138·5°.

0·2150 gave 0·3602 AgCl + AgBr and 0·2453 Ag. Cl = 24·75; Br = 28·68.
$C_8H_6ONCl_2Br$ requires Cl = 25·06 ; Br = 28·26 per cent.

2 : 3-*Dichloro*-4-*bromoaniline* is readily soluble in alcohol, benzene, petroleum, or ether; it crystallises in needles and melts at 77·5°.

0·2374 gave 0·4688 AgCl + AgBr and 0·3198 Ag. Cl = 29·50; Br = 33·27.
$C_6H_4NCl_2Br$ requires Cl = 29·43 ; Br = 33·19 per cent.

1 : 2-*Dichloro*-3-*bromobenzene*.—The amino-group in the preceding compound was removed by the method already described and the product purified by distillation in steam and crystallisation from alcohol. From dilute alcohol, it crystallises in leaflets, but from absolute alcohol in well defined, rhombic plates. It melts at 60° and boils at 243° under 765 mm. pressure.

0·1501 gave 0·3130 AgCl + AgBr and 0·2131 Ag. Cl = 30·75; Br = 35·79.
$C_6H_3Cl_2Br$ requires Cl = 31·38 ; Br = 35·40 per cent.

1 : 3-*Dichloro*-2-*bromobenzene*.

m-Bromoacetanilide was chlorinated in glacial acetic acid solution and the two anilides which resulted were separated exactly as in the case of the preceding compound.

2 : 4-*Dichloro*-5-*bromoacetanilide* crystallises in short prisms and melts at 192°.

0·2280 gave 0·3774 AgCl + AgBr and 0·2574 Ag. Cl = 24·72; Br = 27·88.
$C_8H_6ONCl_2Br$ requires Cl = 25·06 ; Br = 28·26 per cent.

2 : 4-*Dichloro*-5-*bromoaniline* crystallises in flattened prisms, melts at 86°, and distils at 163° under 16 mm. pressure.

0·2436 gave 0·4811 AgCl + AgBr and 0·3269 Ag. Cl = 28·77; Br = 34·53.
$C_6H_4NCl_2Br$ requires Cl = 29·43 ; Br = 33·19 per cent.

The constitution of this aniline was proved by removing the amino-group when 1 : 3-dichloro-4-bromobenzene was obtained.

2 : 4-*Dichloro*-3-*bromoacetanilide* crystallises in prisms from alcohol and in long, fine needles from benzene. It melts at 138°.

0·2013 gave 0·3405 AgCl + AgBr and 0·2322 Ag. Cl = 25·21; Br = 28·59.
$C_8H_6ONCl_2Br$ requires Cl = 25·06 ; Br = 28·26 per cent.

2 : 4-*Dichloro*-3-*bromoaniline* crystallises in plates which melt at 78°. It distils at 172° under 22 mm. pressure.

0·2090 gave 0·4083 AgCl + AgBr and 0·2778 Ag. Cl = 28·69; Br = 33·74.
$C_6H_4NCl_2Br$ requires Cl = 29·43; Br = 33·19 per cent.

1 : 3-*Dichloro*-2-*bromobenzene* is produced on eliminating the amino-group from the last-mentioned compound. It resembles the preceding vicinal dichlorobromobenzene, melts at 65°, and boils at 242° under 765 mm. pressure.

0·1489 gave 0·3117 AgCl + AgBr and 0·2126 Ag. Cl = 31·24; Br = 35·32.
$C_6H_3Cl_2Br$ requires Cl = 31·38; Br = 35·40 per cent.

This compound was also obtained by the following method. Dry *p*-nitroaniline was added to dry benzene and treated with dry chlorine, when much heat was developed and the benzene appeared to boil owing to the escape of hydrogen chloride. The yield of 2 : 6-dichloro-4-nitroaniline is quantitative, and this method of chlorination is more convenient than that employed by Witt (*Ber.*, 1875, 8, 143), namely, treatment of a hydrochloric acid solution of *p*-nitroaniline with potassium chlorate. In the 2 : 6-dichloro-4-nitroaniline, the amino-group was eliminated and the resulting 3 : 5-dichloronitrobenzene reduced by tin and hydrochloric acid. By acetylation of the base, 3 : 5-dichloroacetanilide was prepared and this was treated with one molecular proportion of bromine in presence of fused sodium acetate. On addition of a little water to the acetic acid solution, a solid melting at 215° separated, which, after being twice crystallised from acetic acid, melted constantly at 220°. It formed short prisms.

0·1994 gave 0·3337 AgCl + AgBr and 0·2272 Ag. Cl = 24·69; Br = 28·75
$C_8H_6ONCl_2Br$ requires Cl = 25·06; Br = 28·26 per cent.

On hydrolysis, the anilide yielded an aniline which was purified by distillation in steam and crystallisation from alcohol. This base crystallised in rather long needles and melted at 129°.

0·2099 gave 0·4130 AgCl + AgBr and 0·2812 Ag. Cl = 29·17; Br = 33·75.
$C_6H_4NCl_2Br$ requires Cl = 29·43; Br = 33·19 per cent.

From this aniline by elimination of the amino-group 1 : 3-dichloro-2-bromobenzene was obtained.

1-*Chloro*-2 : 6-*dibromobenzene*.

From *m*-chloroacetanilide, by bromination, there was first prepared 3-chloro-4-bromoacetanilide in pure condition, and from this by treatment with one molecular proportion of bromine, a mixture of the unsymmetrical and vicinal chlorodibromoacetanilides resulted. These anilides were separated in a precisely similar manner to those described under 1 : 2-dichloro-3-bromobenzene.

3-*Chloro*-4 : 6-*dibromoacetanilide* crystallises in thin prisms and melts at 174°.

0·2593 gave 0·4108 AgCl + AgBr and 0·2562 Ag. Cl = 10·67 ; Br = 48·81.
$C_8H_6ONClBr_2$ requires Cl = 10·82 ; Br = 48·84 per cent.

3-*Chloro*-4 : 6-*dibromoaniline* has been obtained by Wheeler and Valentine (*Amer. Chem. J.*, 1899, **22**, 270). Its constitution is proved by removing the amino-group, when it yields 1-chloro-2 : 4-dibromobenzene.

3-*Chloro*-2 : 4-*dibromoacetanilide* crystallises in prisms melting at 152°.

0·2192 gave 0·3480 AgCl + AgBr and 0·2169 Ag. Cl = 10·75; Br = 49·06.
$C_8H_6ONClBr_2$ requires Cl = 10·82 ; Br = 48·84 per cent.

3-*Chloro*-2 : 4-*dibromoaniline* crystallises in plates which melt at 88°.

0·1772 gave 0·3231 AgCl + AgBr and 0·2016 Ag. Cl = 12·52; Br = 56·05.
$C_6H_4NClBr_2$ requires Cl = 12·42 ; Br = 56·02 per cent.

1-*Chloro*-2 : 6-*dibromobenzene*, obtained from the last-mentioned compound by replacing the amino-group by hydrogen, closely resembles the preceding vicinal chlorodibromobenzenes.

This compound was also obtained from 2 : 6-dibromoaniline, for which I am indebted to Dr. Orton, by replacing the amino-group by chlorine—a reaction which goes very smoothly.

It melts at 69·5° and boils at 265° under 760 mm. pressure.

0·1780 gave 0·3419 AgCl + AgBr and 0·2133 Ag. Cl = 13·17; Br = 59·08.
$C_6H_3ClBr_2$ requires Cl = 13·11 ; Br = 59·14 per cent.

1-*Chloro*-2 : 3-*dibromobenzene*.

m-Bromoacetanilide was treated with one molecular proportion of bromine and the 3 : 4-dibromoacetanilide, which is by far the principal product, was purified by two crystallisations from alcohol. The glacial acetic acid solution of this product was saturated with chlorine and the unsymmetrical and vicinal anilides isolated in exactly the same way as the corresponding chlorobromoanilides.

2-*Chloro*-4 : 5-*dibromoacetanilide* crystallises in needles and melts at 198°.

0·2091 gave 0·3343 AgCl + AgBr and 0·2090 Ag. Cl = 11·25; Br = 48·67.
$C_8H_6ONClBr_2$ requires Cl = 10·82 ; Br = 48·84 per cent.

2-*Chloro*-4 : 5-*dibromoamiline* melts at 93° and crystallises in flattened needles.

0·2060 gave 0·3757 AgCl + AgBr and 0·2344 Ag. Cl = 12·51; Br = 56·08.
$C_6H_4NClBr_2$ requires Cl = 12·42; Br = 56·02 per cent.

Replacement of the amino-group by hydrogen gave 1-chloro-3 : 4-dibromobenzene.

2-*Chloro*-3 : 4-*dibromoacetanilide* crystallises in fine needles from benzene and melts at 146°.

0·2287 gave 0·3649 AgCl + AgBr and 0·2275 Ag. Cl = 10·84; Br = 49·23.
$C_8H_6ONClBr_2$ requires Cl = 10·82; Br = 48·84 per cent.

2-*Chloro*-3 : 4-*dibromoaniline* crystallises in plates and melts at 91°.

0·2165 gave 0·3928 AgCl + AgBr and 0·2450 Ag. Cl = 12·13; Br = 55·87.
$C_6H_4NClBr_2$ requires Cl = 12·42; Br = 56·02 per cent.

1-*Chloro*-2 : 3-*dibromobenzene*, obtained from the preceding compound by removal of the amino-group, closely resembles the other vicinal chlorodibromobenzenes. It melts at 73·5° and boils at 142° under 23 mm. and at 264° under 754 mm. pressure.

0·2029 gave 0·3881 AgCl + AgBr and 0·2415 Ag. Cl = 12·69; Br = 59·57.
$C_6H_3ClBr_2$ requires Cl = 13·11; Br = 59·14 per cent.

I have much pleasure in stating that Dr. Orton drew my attention to the fact that the chlorodibromo- and dichlorobromo-benzenes had not been prepared, and in acknowledging the help I have received from the advice and criticism of both Dr. Chattaway and Dr. Orton.

The examination of these compounds is being continued, and the preparation of some of the chlorobromotoluenes, several of which have been obtained, has also been undertaken.

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CXXXVII.—*Experiments on the Production of Optically Active Compounds from Inactive Substances.*

By J. B. COHEN and C. E. WHITELEY.

THE withdrawal of one of us from this research has made it desirable to publish the results of our experiments as far as they have gone.

In addition to the three well known methods devised by Pasteur for obtaining optically active compounds from inactive asymmetric

materials, many new processes have in recent years been proposed. These methods may be said to consist in subjecting the material to an unsymmetrical action of either a physical or chemical nature.

Among the physical processes may be mentioned the crystallisation of the inactive material in a magnetic field which Pasteur tried without success and which has since been repeated by Boyd (Landolt, *Optische Drehungsvermögen*, p. 111) and others with similar results. Kipping and Pope have employed the method of crystallisation of a racemic compound from a solvent containing an active substance in solution (Proc., 1898, **14**, 113) and obtained evidence of its effect in promoting the deposition of a larger proportion of one of the enantiomorphs. Among the chemical processes are the following. The selective hydrolysis of glucosides was effected by E. Fischer, by means of enzymes (*Zeit. physiol. Chem.*, **26**, 60); the fractional esterification of an inactive acid in combination with an active alcohol, or the reverse process, namely, the partial hydrolysis of an ester composed of an inactive acid and an active alcohol, was successfully employed by Marckwald and McKenzie (*Ber.*, 1899, **32**, 2130; 1901, **34**, 469) and Walden (*Ber.*, 1899, **32**, 3617); the rate of hydrolysis of cane sugar effected by *d*- and *l*-camphoric acid was investigated by E. Fischer with negative results (*Ber.*, 1899, **32**, 3617). The formation of a new asymmetric carbon atom under asymmetrical conditions has also been studied by E. Fischer in the synthesis of the sugars. It is this process which has especially attracted our attention. E. Fischer (*Annalen*, 1892, **270**, 64) has shown that in the synthesis of one sugar from another by the addition of hydrogen cyanide to the lower member, a new asymmetric carbon atom is introduced which may give rise to two stereoisomeric compounds represented as follows:

$$-C\lessdot^{O}_{H} + HCN = \begin{matrix} H \\ | \\ -C-OH \\ | \\ CN \end{matrix} \quad \text{and} \quad \begin{matrix} H \\ | \\ HO-C- \\ | \\ CN \end{matrix}$$

Although the two new groups are optical antipodes, the two isomerides are not necessarily so as a whole, and are not always produced in equal quantities. Fischer has found, for example, that *d*-glucose forms two cyanohydrins in very unequal quantities (*loc. cit.*), whilst in the case of *d*-mannose only one of the two possible cyanohydrins is produced (Hartmann, *Annalen*, 1892, **272**, 190). It is clear, therefore, that the asymmetric molecule exerts its influence on the space configuration of the newly added asymmetric carbon group.

In these examples, it is impossible to determine exactly the influence of the active part of the original molecule on the activity of the new group, seeing that the latter cannot be detached from the molecule. As the formation of active substances in living organisms is probably

closely connected with their production from other active substances from which they are afterwards removed, the idea occurred to us to attempt to produce a new asymmetric carbon atom in an already active compound from which the originally active group could be subsequently detached.

A number of reactions readily presented themselves, such as the reduction, bromination, or hydroxylation of esters composed of an unsaturated acid and an active alcohol, or the reduction of a ketonic ester of an active alcohol, the alcohol being afterwards removed by hydrolysis.

These reactions may be represented as follows: (X stands for an atom or group not being hydrogen, A indicates the active alkyl or aryl group, and C the new asymmetric carbon atom):

1. $\cdot CH{:}CH\cdot CO_2A \longrightarrow \cdot CHX\cdot CHX\cdot CO_2A \longrightarrow \cdot CHX\cdot CHX\cdot CO_2H$
2. $\cdot CH{:}CX\cdot CO_2A \longrightarrow \cdot CH_2\cdot CHX\cdot CO_2A \longrightarrow \cdot CH_2\cdot CHX\cdot CO_2H$
3. $\cdot CO\cdot CO_2A \longrightarrow \cdot CH(OH)\cdot CO_2A \longrightarrow \cdot CH(OH)\cdot CO_2H$

Under 1, we have prepared the bromine derivatives of the amyl and menthyl cinnamates, and of dicinnamyltartaric acid and examined the action of various reagents on the dibromo-compounds.

All these experiments, after a considerable loss of time, had to be abandoned. Although the dibromo-derivatives of amyl and menthyl cinnamates and of dicinnamyltartaric acid could be readily obtained in a state of purity, they could not be directly hydrolysed without removing bromine, and all attempts to replace bromine by hydroxyl failed.

Under 2, we have studied the reduction of the menthyl esters of mesaconic acid and α-methylcinnamic acid.

Under 3, we have investigated the reduction of menthyl pyruvate.

The results in all cases have been of a negative character, in spite of every care to avoid possible racemisation by conducting the critical steps in the reactions at the ordinary temperature.

Experimental.

Amyl Cinnamate.

A few preliminary experiments were made with this compound with the object of introducing asymmetric carbon atoms into the acid portion of the ester in its combination with active amyl alcohol. The substance was prepared by heating together equal weights of cinnamic chloride and ordinary amyl alcohol until hydrogen chloride ceased to be evolved. The product was then washed with water, dried over

calcium chloride, and distilled in a vacuum. It boiled at 186—188° under 20 mm. pressure; d 20°/20° = 0·975.

It is a colourless oil with a faint odour of amyl alcohol. In order to obtain the phenylglycerate, the amyl cinnamate was treated with dilute permanganate, but even in a freezing mixture it underwent oxidation to benzaldehyde and benzoic acid, and no trace of the dihydroxy-compound could be detected. It was then converted into the dibromo-derivative by adding one molecular equivalent of bromine dissolved in chloroform. The bromine was readily absorbed and the product, when purified, formed a colourless oil. All attempts to replace bromine by hydroxyl failed.

Menthyl Cinnamate.

This ester was prepared with the same object as the amyl ester, and with equally fruitless results. It was obtained by heating together in the oil-bath at 140° equivalent quantities of cinnamyl chloride and menthol, and purified by adding sodium carbonate and distilling in steam. The residue was extracted with ether, dehydrated over calcium chloride, and the ether removed by evaporation. The ester formed a light yellow, viscid liquid which did not crystallise. It was then converted into the dibromo-compound by the addition of the equivalent quantity of bromine in chloroform. The colour of the bromine slowly disappeared and after removal of the chloroform the dibromo-compound crystallised. After recrystallisation from glacial acetic acid, it formed colourless needles and melted at 84°. On analysis:

0·220 gave 0·1697 AgBr. Br = 36·1.

$C_{19}H_{26}O_2Br_2$ requires Br = 35·9 per cent.

We were unsuccessful in all our attempts to replace bromine by hydroxyl, ethoxyl, or acyloxyl groups.

Tetrabromodicinnamyltartaric Acid.

Dicinnamyltartaric anhydride is readily prepared by the method described by Freundler (*Ann. Chim. Phys.*, 1894, [vii], 3, 486). It was brominated in chloroform solution and the liquid product remaining, after removing chloroform, crystallised on the addition of a little water, forming colourless crystals of tetrabromodicinnamyltartaric acid. It was completely decomposed with alkalis, and with ammonia deposited crystals melting at 119°, which were identified as monobromocinnamide, $C_6H_5{\cdot}CBr{:}CH{\cdot}CO{\cdot}NH_2$.

0·1316 gave 0·1073 AgBr. Br = 34·7.

C_9H_8ONBr requires Br = 35·4 per cent.

No hydroxy-derivative could be obtained from this substance.

Menthyl Pyruvate.

Thirty-one grams of pyruvic acid and 55 grams of menthol were heated under diminished pressure on the water-bath with a reflux condenser. The product was then distilled in a vacuum and the ester collected at 136—140° under 22 mm. pressure. d 11·5°/4° = 0·9917; $[\alpha]_D^{11.5°}$ −181·7°. On analysis:

0·3153 gave 0·1249 CO_2 and 0·112 H_2O. C = 68·85; H = 9·96.

$C_{13}H_{22}O_3$ requires C = 69·03; H = 9·73 per cent.

Menthyl Lactate.

After several trials with different reducing agents and under different conditions, the following process was found to give the most satisfactory result.

Menthyl pyruvate (5—10 grams) was reduced with constant stirring in the cold with four times the theoretical quantity of glacial acetic acid and zinc dust, the latter being added at intervals during 5—6 hours. The stirring was continued for double that time. The product was filtered and washed with dry ether. The filtrate was shaken in a separating funnel with water and excess of barium carbonate to remove the acetic acid. When all effervescence ceased, the product was filtered, and the ethereal layer removed from the filtrate and evaporated to a syrupy consistency in a vacuum at the ordinary temperature. The syrupy residue was mixed with the theoretical quantity of potassium hydroxide dissolved in methyl alcohol and left overnight in a vacuum at the ordinary temperature, when complete hydrolysis was effected. Water was added to the dry product, which was extracted with ether to remove menthol. The aqueous solution of potassium lactate, which was free from pyruvate, was made strongly acid, evaporated to a gummy mass in a vacuum at the ordinary temperature, and the free lactic acid extracted several times with ether. On evaporation of the ether, the residue was boiled with water and zinc carbonate, and, from the filtrate, crystals of zinc lactate separated. Ten grams of menthyl pyruvate yielded about 3·5 grams of zinc lactate, or 50 per cent. of the calculated amount. The air-dried salt was analysed, with the following result:

1·4412, at 105°, lost 0·2612 H_2O. H_2O = 18·12.

0·6032 gave 0·2017 ZnO. Zn = 22·00.

$(C_3H_5O_3)_2Zn,3H_2O$ requires H_2O = 18·17; Zn = 21·98 per cent.

A saturated solution of zinc lactate in a 500 mm. tube gave a rotation of only 1′.

Menthyl Mesaconate.

The mesaconic acid was prepared by Fittig's method by the action of bromine on an ether-chloroform solution of citraconic acid. To prepare the mesaconyl chloride, 10·8 grams of the acid were mixed with 34·8 grams of phosphorus pentachloride, and heated on the water-bath until hydrogen chloride ceased to be evolved. The phosphorus oxychloride was then distilled off on the water-bath under diminished pressure, and the remainder (9·8 grams) consisted of the acid chloride. This was mixed with the theoretical quantity of menthol (18·3 grams) and heated to 130° on the oil-bath. The product was made alkaline with sodium carbonate solution and distilled in steam. The residue was extracted with ether and the ether evaporated. The product consisted of a thick liquid; d 17·6°/4° = 0·9904; $[\alpha]_D^{17·6°}$ −91·05°. On analysis:

0·218 gave 0·5858 CO_2 and 0·2057 H_2O. C = 73·28; H = 10·48.
$C_{25}H_{42}O_4$ requires C = 73·89; H = 10·34 per cent.

Menthyl Pyrotartrate.

23·6 grams of the mesaconic ester were dissolved in alcohol, and 50 grams of the aluminium-mercury couple added in small portions at a time, a few drops of water being occasionally introduced. The operation lasted 6 weeks. The reduced product was then filtered, and further extracted from the excess of the couple and of aluminium hydroxide by means of hot alcohol. On evaporation of the alcohol, the liquid product, which had d 11·8°/4° = 0·978, and $[\alpha]_D^{11·8°}$ −71·6°, was analysed, with the following results:

0·1830 gave 0·4910 CO_2 and 0·1769 H_2O. C = 73·17; H = 10·82.
$C_{25}H_{44}O_4$ requires C = 73·45; H = 10·88 per cent.

The product was treated with the theoretical quantity of methyl alcoholic potash in the cold to effect hydrolysis, and then extracted with ether to remove the menthol. The solution of potassium pyrotartrate was then acidified with hydrochloric acid and extracted with ether. On evaporating the ether, crystals of pyrotartaric acid separated, and had the correct melting point, namely, 112—113°. 7·1 grams of the menthyl pyrotartrate gave 2·37 grams of pure pyrotartaric acid. The acid was analysed, with the following results:

0·1581 gave 0·263 CO_2 and 0·0855 H_2O. C = 45·37; H = 6·04.
$C_5H_8O_4$ requires C = 45·42; H = 6·06 per cent.

1·68 grams were dissolved in water and made up to 10 c.c. The

rotation in a 100 mm. tube was $-5{\cdot}5'$. The substance was further purified by neutralising with potash and extracting repeatedly with ether to remove any traces of menthol. 1·8 grams in 10 c.c. now gave a rotation of $4{\cdot}4'$. This small rotation can scarcely be regarded as undoubted proof of the formation of an optically active compound.

Menthyl α-Methylcinnamate, $C_6H_5{\cdot}CH{:}C(CH_3){\cdot}CO_2{\cdot}C_{10}H_{19}$.

The α-methylcinnamic acid was prepared by the method described by Edeleano (*Ber.*, 1887, 20, 618). It was converted into the chloride by heating with an equal weight of phosphorus trichloride on the water-bath for an hour. The liquid was decanted from solid phosphorus compounds and the residue rinsed out with ether, which was added to the clear liquid. On distilling off the ether, the acid chloride solidified, and after recrystallisation from ether melted at 48—50°. Ten grams of acid yielded 8 grams of acid chloride. An equal weight of menthol (8 grams) was added to the acid chloride and the mixture heated in the oil-bath at 120—130° for an hour. The product was made alkaline with sodium carbonate solution and distilled in steam until free menthol ceased to distil over. The residue was extracted with ether and dehydrated over calcium chloride. On removing the ether, the residue (12 grams) solidified. It was purified by dissolving in methyl alcohol, from which it crystallised in large tablets melting at 50°. On analysis:

0·1568 gave 0·4567 CO_2 and 0·1314 H_2O. C = 79·43; H = 9·38.
$C_{20}H_{28}O_2$ requires C = 79·92; H = 9·42 per cent.

The rotation in a 30·48 mm. tube at 58° was $-20°44'$. After various reducing reagents had been tried unsuccessfully, the aluminium-mercury couple was finally adopted, although its action is very slow.

Five grams of the ester were reduced by a large excess of the couple (40 grams) during 3 months, and 4 grams of pure crystallised menthyl α-methylhydrocinnamate melting at 37° were obtained. The purity of the product was determined by comparison with some of the pure menthyl ester prepared directly from α-methylhydrocinnamic acid. Four grams of the acid were warmed on the water-bath with 5 grams of phosphorus pentachloride, and the phosphorus oxychloride was then removed by distilling under reduced pressure from the water-bath. The residue distilled at 160° under 30 mm. pressure. The distillate consisted of a pale yellow liquid which did not solidify. It was heated in the oil-bath at 140° with an equal weight of menthol and distilled in steam with the addition of sodium carbonate solution to remove menthol. The residue was extracted with ether and dehydrated over calcium chloride. On removing the ether, the menthyl ester solidified,

and after recrystallisation from methyl alcohol melted at 36—38°, in agreement with the above result.

The menthyl ester obtained by reduction with the couple was hydrolysed with alcoholic potash in the cold as described in the other cases, and 0·75 gram of pure acid (m. p. 36—38°) dissolved in chloroform and the rotation determined in a 200 mm. tube. The rotation was +4′, which is of the same order as that observed in the other cases, and too small to be looked upon as positive evidence of optical activity. Our thanks are due to Dr. T. S. Patterson for kindly placing his polarimeter at our disposal.

Reduction of the α-Methylcinnamic Esters.

The great difference shown in the rate at which methyl and menthyl cinnamate undergo reduction on the one hand, and menthyl α-methylcinnamate on the other, suggested the possibility that the additional methyl group in the side-chain of the acid radicle retarded the action of the couple. In order to obtain further evidence, the methyl, ethyl, propyl, and *iso*propyl esters of α-methylcinnamic acid were prepared. The first three were obtained by Fischer and Speier's method, and the last by the action of *iso*propyl iodide on the silver salt of the acid.

The specific gravities and melting and boiling points of these esters are as follows :

Ester.	*d* 15°/15°.	M. p.	B. p.
Methyl	—	39°	—
Ethyl..... ..	1·049	—	155—160° (30 mm.).
Propyl	1·027	—	162—165 (25 mm.).
*iso*Propyl	1·026	—	155—160 (20 mm.).

The method for determining the rate of reduction was to reduce 1 gram of the methyl ester and a proportionate quantity of the others in ethyl alcoholic solution with excess of the couple (1 gram) during the same period of time, to remove the alcohol, hydrolyse the product, and titrate the alkaline solution with standard permanganate, which rapidly oxidises the unsaturated acid but not the reduced compound. No difference could, however, be detected between the esters. They were all readily and completely reduced.

Our thanks are due to Mr. C. P. Finn for his help in carrying out some of these experiments on the reduction of the esters.

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CXXXVIII.—*The Products of the Action of Fused Potassium Hydroxide on Dihydroxystearic Acid.*

By Henry Rondel Le Sueur.

Two papers communicated to the Society by Dr. Crossley and the author (Trans., 1899, **75**, 161; 1900, **76**, 83) contain details of experiments made in order to devise a method by which the constitution of fatty acids might be determined. In this process, the fatty acid is first converted into an unsaturated acid with the double bond between the α- and β-carbon atoms and this acid is then oxidised with potassium permanganate in alkaline solution, whereby a dihydroxy-acid is produced,

$$R\cdot CH{:}CH\cdot CO_2H \longrightarrow R\cdot CH(OH)\cdot CH(OH)\cdot CO_2H,$$

which on further oxidation with potassium dichromate and dilute sulphuric acid is converted into a saturated acid containing two carbon atoms less than the original acid and oxalic acid or its oxidation products.

$$R\cdot CH(OH)\cdot CH(OH)\cdot CO_2H \rightarrow R\cdot CO_2H + CO_2H\cdot CO_2H\ (\rightarrow CO_2 + H_2O).$$

The final substance is not invariably an acid; for instance, if the original acid is of the type $R_2CH\cdot CH_2\cdot CO_2H$, the final oxidation product will be a ketone of the type R_2CO (Trans., 1899, **75**, 164).

In this method, the second oxidation, that with potassium dichromate and dilute sulphuric acid, is carried out in an acid solution, and provided the dihydroxy-acid is soluble in such a solution, the method works well; if, however, it is insoluble, then the oxidation is very slow, and only a small part of the dihydroxy-acid is completely oxidised. It was thought that in such cases fusion of the dihydroxy-acid with potassium hydroxide might serve the same purpose as the oxidation with potassium dichromate and dilute sulphuric acid, and the work described in this paper was undertaken in order to see whether this assumption was correct. Dihydroxystearic acid was chosen because it can be obtained fairly easily in large quantities and is insoluble in water; it was also hoped that the results obtained would furnish evidence from which the formula of dihydroxystearic acid and consequently that of oleic acid might be definitely established. For instance, using the generally accepted formula for the acid, oleic acid, $CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$, on oxidation with potassium permanganate, should give dihydroxystearic acid,

$$CH_3\cdot[CH_2]_7\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H,$$

which, on fusion with potassium hydroxide, would be broken up, yielding molecular quantities of pelargonic acid, $CH_3{\cdot}[CH_2]_7{\cdot}CO_2H$, and azelaic acid, $CO_2H{\cdot}[CH_2]_7{\cdot}CO_2H$, as the sole initial products. The pelargonic and azelaic acids might suffer further decomposition and the author has satisfied himself that such does actually happen in the case of the latter.

The results obtained were unexpected, for instead of the final product being an acid or acids containing fewer carbon atoms than the original substance, the main product was an acid containing the same number of carbon atoms, which clearly showed that, whatever may be the correct formula of dihydroxystearic acid, the main decomposition did not take place between the two carbon atoms to which the hydroxyl groups are attached. The result of the work described in this communication therefore apparently gives no clue to the constitution of dihydroxystearic acid; further investigation of the dibasic acid obtained may, however, furnish some evidence in this direction.

The fusion of dihydroxystearic acid with potassium hydroxide was first carried out at 270—275°, and the substances isolated from the product were found to consist mainly of an oil boiling at 280—300° under 50 mm. pressure, together with small quantities of pelargonic and azelaic acids. The effect of carrying out the fusion at a somewhat lower temperature was next tried, when, as is described below, the following substances were isolated: A dibasic acid, $C_{18}H_{34}O_5$, melting at 111—111·5°; an acid, $C_{18}H_{34}O_3$, melting at 78·5—79°; pelargonic acid; and azelaic acid. The first of these was obtained in a 58 per cent. yield of that theoretically obtainable and the other three only in small quantities.

That the acid $C_{18}H_{34}O_5$ (m. p. 111—111·5°) is dibasic is clearly shown from the analysis of its salts, its titration with standard alkali, the determination of the molecular weight of its ethyl ester by the freezing point method, and also from its capability of forming an amic acid and a diamide. That it is also a monohydroxy-acid is shown from the fact that it yields a monoacetyl derivative on treatment with acetic anhydride or acetyl chloride. No mention could be found of the previous existence of this acid.

Analyses of the acid $C_{18}H_{34}O_3$ (m. p. 78·5—79°) and of its sodium salt gave numbers which agree closely with the calculated values for the formulæ assigned to them. The acid may be regarded as an internal anhydride, formed by the elimination of one molecule of water from a molecule of dihydroxystearic acid:

$$CO_2H{\cdot}C_{15}H_{31}\begin{cases}CH{\cdot}OH\\ |\\ CH{\cdot}OH\end{cases} \longrightarrow CO_2H{\cdot}C_{15}H_{31}\begin{cases}CH\\ |\\ CH\end{cases}O.$$

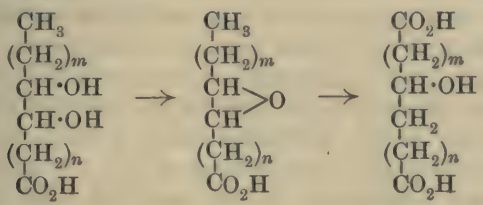
It was thought that such an acid would be reconverted into dihydr-

oxystearic acid by boiling with dilute acids or alkalis, but experiments carried out in this direction have so far proved unsuccessful.

By the distillation of dihydroxystearic acid under reduced pressure, Saytzeff (*J. pr. Chem.*, 1886, [ii], **33**, 313) obtained an acid melting at 77—79° and solidifying at 69—70°, to which he assigned the formula $C_{18}H_{34}O_3$. He regarded it as an anhydride of dihydroxystearic acid formed as described above. But this acid must have been impure, because the numbers which Saytzeff obtained on analysis do not agree at all closely with those calculated for the formula $C_{18}H_{34}O_3$, the mean of four analyses giving 70·91 per cent. of carbon, whereas the calculated amount is 72·49 per cent. It must, however, be stated that the sodium and silver salts on analysis gave numbers which agree well with those calculated for a monobasic acid of the formula $C_{18}H_{34}O_3$.

Albitzky (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 76) has described glycidic acids of similar composition, obtained by the action of barium hydroxide on the chlorohydroxystearic acids.

The formation of a monohydroxydicarboxylic acid from a dihydroxymonocarboxylic acid is not easy to explain, unless it is assumed that the acid $C_{18}H_{34}O_3$ is first formed and that this is immediately oxidised to the acid $C_{18}H_{34}O_5$. Thus



Experimental.

Preparation of Dihydroxystearic Acid.—The acid was prepared by the oxidation of oleic acid with potassium permanganate in alkaline solution, as recommended by Saytzeff (*loc. cit.*). Eighty-four grams of oleic acid (Kahlbaum's pure acid) were dissolved in 1500 c.c. of water containing 33 grams of potassium hydroxide, the solution was cooled to 0°, and a cold solution of 84 grams of potassium permanganate in 1500 c.c. of water gradually added, the mixture being well stirred by means of a turbine and its temperature maintained below 10°. The whole was allowed to remain overnight, filtered from the separated manganese dioxide, and acidified with dilute sulphuric acid, when a very voluminous, white precipitate of dihydroxystearic acid separated out. This was filtered off, dried on a porous plate, and extracted with

a small volume of ether in order to remove any unoxidised oleic acid. The residue (insoluble in ether) was recrystallised from rectified spirit until its melting point was constant, when 45 grams of pure dihydroxystearic acid were obtained, the yield amounting to 48 per cent. of that theoretically possible.

Melting Point of Dihydroxystearic Acid.—Various temperatures have been given as the correct melting point of pure dihydroxystearic acid. Saytzeff (*loc. cit.*), Hazura (*Monatsh.*, 1888, **9**, 186), and others, state that the acid melts at 136·5°; Edmed (Trans., 1898, **73**, 629) gives 134° as the melting point, Gröger (*Ber.*, 1889, **22**, 620) gives 130·5—131·5°, and lastly, Freundler (*Bull. Soc. Chim.*, 1885, [iii], **13**, 1052), who separated the acid into its optical isomerides, states that it melts at 131°. In view of these conflicting statements, it was deemed advisable to make every effort to ascertain the true melting point of the pure acid. The dihydroxystearic acid, obtained as described above, after two recrystallisations from rectified spirit melted at 130·5—131° (uncorr.), and after three further recrystallisations still melted at this temperature. On analysis:

0·1500 gave 0·3754 CO_2 and 0·1536 H_2O. C = 68·25; H = 11·38.
$C_{18}H_{36}O_4$ requires C = 68·35; H = 11·39 per cent.

The acid was then boiled with a large volume of water, in which it is insoluble, whereas the higher hydroxylated acids, such as sativic acid (tetrahydroxystearic acid), are somewhat soluble, and again recrystallised from rectified spirit, when it still melted at 130·5—131° (uncorr.). It was next boiled with ether, in which it is slightly soluble, and the ethereal solution filtered off from the undissolved portion. Both this undissolved residue and the acid obtained by evaporation of the ethereal solution melted at exactly the same temperature, namely, 130·5—131°. The dihydroxystearic acid, which was obtained by the author from the oxidation of the unsaturated acids of the oil of *Carthamus tinctorius*, also melted at this temperature (*J. Soc. Chem. Ind.*, 1900, **19**, 104). On applying the usual method for correcting the melting point of a substance, 131·5—132° is obtained as the corrected melting point of pure dihydroxystearic acid.

Calcium Salt of Dihydroxystearic Acid.—Saytzeff (*loc. cit.*) states that calcium dihydroxystearate, after drying in a desiccator, contains 1 mol. of water of crystallisation; Edmed (*loc. cit.*), on the other hand, states that the dried salt contains 3 mols., but from the following results it will be seen that the air-dried salt contains only 1 mol. of water of crystallisation. The salt was prepared by adding an aqueous solution of the potassium salt of the acid to an aqueous solution of calcium chloride. On analysis:

0·4876, air-dried salt, at 135° lost 0·0134 H_2O. $H_2O = 2·74$.
0·4716 salt dried at 135° gave 0·1000 $CaSO_4$. $Ca = 6·23$.
$(C_{18}H_{35}O_4)_2Ca,H_2O$ requires $H_2O = 2·62$ per cent.
$(C_{18}H_{35}O_4)_2Ca$,, $Ca = 5·97$,,

Fusion of Dihydroxystearic Acid with Potassium Hydroxide.—Five grams of dihydroxystearic acid, 25 grams of pure potassium hydroxide, and sufficient water to form a thick paste, were well mixed together in a nickel crucible and heated in a metal bath. At 200°, the mass completely liquefied, and at 250° it turned slightly brown in colour and evolved a small amount of hydrogen. The temperature was then raised to 270—275° and maintained at this point until the rapid evolution of hydrogen which at first took place had ceased. The product was then cooled, dissolved in water, acidified with dilute sulphuric acid, and subjected to steam distillation. The distillate contained pelargonic acid, which was identified by the melting point of its crystalline zinc salt. The residue in the flask contained a dark oil, which was filtered off (filtrate = A) from the mother liquor, dried in a vacuum desiccator, treated with ether, and the ethereal solution (filtered from a small amount of insoluble residue) evaporated, when 1·2 grams of an oil which distilled without decomposition at 280—300° under 50 mm. pressure were obtained. Azelaic acid was isolated from the aqueous filtrate A and identified by its melting point (106°) and analysis.

The effect of carrying out the fusion at a somewhat lower temperature was next tried, when it was found that no oil was produced, but that the acids left in the flask after steam distillation solidified to a hard mass, which at first was thought to be unchanged dihydroxystearic acid. This, however, was soon found not to be the case, as the substance is readily soluble in ether, in which dihydroxystearic acid is only slightly soluble, and on extracting the solid fractionally with chloroform two acids were obtained melting respectively at 111—111·5° and 78·5—79°. In order to obtain larger quantities of these two substances, 250 grams of dihydroxystearic acid were fused with potassium hydroxide in quantities of 40 grams at a time, the fusion being carried out as follows: 40 grams of dihydroxystearic acid, 200 grams of pure potassium hydroxide, and sufficient water to form a thick paste were well mixed in a nickel crucible and gradually heated in a metal bath, the mass being vigorously stirred the whole time. At 200°, the mass liquefied and there was much frothing; the temperature was then raised to 250° and maintained at this point until the frothing ceased, which took place after 20 minutes, during which time only traces of hydrogen were evolved. If the heating be continued, much hydrogen is evolved and the mass darkens. It is necessary that the fusion should be stopped the moment this second action sets in, otherwise the result-

ing substances are those described on page 1317. The fused product was dissolved in water, acidified with dilute sulphuric acid, and the liberated acids separated from the mother liquor and washed with boiling water.

The whole of the mother liquor was extracted four times with a large volume of ether, when, on evaporation of the ethereal solution, 10 grams of a solid residue were obtained, which was readily soluble in hot water and crystallised out on cooling in large plates which melted at 105—106° and had all the properties of azelaic acid. On analysis:

0·1550 gave 0·3272 CO_2 and 0·1182 H_2O. C = 57·57; H = 8·47.
$C_9H_{16}O_4$ requires C = 57·44; H = 8·51 per cent.

On cooling, the acids liberated by sulphuric acid solidified to a hard mass, which was powdered, dried in a vacuum desiccator, and extracted with cold chloroform; the products soluble and insoluble in this solvent were then investigated.

Product Insoluble in Chloroform.

The portion insoluble in chloroform was recrystallised from acetic acid until its melting point was no longer changed (111—111·5°).

Of the pure acid, 120 grams were obtained from 200 grams of dihydroxystearic acid, a yield which corresponds to 58 per cent. of that theoretically obtainable. On analysis:

0·1422 gave 0·3396 CO_2 and 0·1324 H_2O. C = 65·13; H = 10·34.
0·1340 „ 0·3210 CO_2 „ 0·1256 H_2O. C = 65·33; H = 10·41.
$C_{18}H_{34}O_5$ requires C = 64·45; H = 10·30 per cent.

This acid is insoluble in cold water, but melts in boiling water. Its alcoholic solution gives a well-marked effervescence with a dilute solution of sodium carbonate or sodium hydrogen carbonate in the cold. It dissolves slowly in a cold solution of potassium hydroxide, and the solution thus produced does not affect potassium permanganate in the cold and reduces it only slightly on heating; it is without effect on Fehling's solution. The acid is somewhat readily soluble in alcohol, ether, ethyl acetate, or acetone in the cold, and also in hot acetic acid. It is insoluble in benzene, chloroform, or light petroleum in the cold, but dissolves readily in the former on heating. It crystallises from dilute alcohol or dilute acetic acid in aggregates of long, flat needles melting at 111—111·5°.

Titration of the Acid.—The acid was dissolved in alcohol which had been previously neutralised and the solution titrated with a decinormal solution of potassium hydroxide.

(i). 0·4172 required 25·23 c.c., using phenolphthalein as indicator.
(ii). 0·5614 „ 34·2 c.c. „ litmus „

One gram of the acid therefore requires (i) 60·5 c.c.; (ii) 60·9 c.c., the calculated amount for 1 gram of a dibasic acid, $C_{18}H_{34}O_5$, being 60·6 c.c.

The *sodium* salt was obtained as a hard mass of no very definite crystalline structure and could not be recrystallised from alcohol or water, owing to its great solubility. These remarks also apply to the neutral and acid potassium salts.

The *silver* salt was thrown down as a white, curdy precipitate when a solution of the sodium salt was poured into excess of a warm solution of silver nitrate. On analysis:

0·2310 gave 0·3360 CO_2, 0·1238 H_2O, and 0·0904 Ag. C = 39·66; H = 5·95; Ag = 39·13.
0·1344 gave 0·0534 Ag. Ag = 39·73.
$C_{18}H_{32}O_5Ag_2$ requires C = 39·70; H = 5·88; Ag = 39·70 per cent.

The *barium* salt was obtained as a white precipitate on the addition of a solution of the sodium salt to a solution of barium chloride. The salt was dried at 100° and analysed:

0·2226 gave 0·1104 $BaSO_4$. Ba = 29·20.
$C_{18}H_{32}O_5Ba$ requires Ba = 29·52 per cent.

The *calcium* salt was obtained as a white, gelatinous precipitate on the addition of a solution of the sodium salt to a solution of calcium chloride. The amount of water present in the air-dried salt was found to vary in different samples. In one case, numbers were obtained which agreed with those required for a salt of the formula $C_{18}H_{32}O_5Ca,3H_2O$. The air-dried salt loses the greater part of its water in a vacuum, but the last traces are only expelled at 155°. The salt was therefore dried at 155°, until no further loss occurred, and analysed:

0·2664 gave 0·0972 $CaSO_4$. Ca = 10·73.
0·2176 ,, 0·0798 $CaSO_4$. Ca = 10·78.
$C_{18}H_{32}O_5Ca$ requires Ca = 10·87 per cent.

Precipitates were obtained on the addition of an aqueous solution of the sodium salt of the acid to solutions of salts of mercury, copper, lead, manganese, iron, zinc, magnesium, cobalt, or nickel.

Ethyl Ester, $C_{18}H_{32}O_5(C_2H_5)_2$.—The calculated quantity of ethyl iodide was added to the dry silver salt, which was covered with anhydrous ether in a flask attached to a reflux condenser and the whole heated on the water-bath for 2¼ hours. The resulting ethereal solution, which was of a bright yellow colour, due to finely divided silver iodide held in suspension, was evaporated, and the residual oil purified by distillation under reduced pressure. On analysis:

0·1526 gave 0·3816 CO_2 and 0·1490 H_2O. C = 68·20; H = 10·85.
$C_{22}H_{42}O_5$ requires C = 68·39; H = 10·88 per cent.

It was also prepared directly from the acid as follows. Fifty c.c. of concentrated sulphuric acid were gradually added to a solution of 10 grams of the acid in 100 c.c. of absolute alcohol and the mixture allowed to remain at the ordinary temperature for 4 days and then heated on the water-bath for 3 hours. The product was poured into water, extracted with ether, the ethereal solution well washed with water, and after evaporation of the solvent, the residual liquid was purified by fractional distillation under reduced pressure, when 7·2 grams, boiling at 268—274° under 31 mm. pressure, were obtained. The ester thus produced had a slight acid reaction, due no doubt to the presence of a trace of free acid or acid ester.

The ester is a very faintly yellow, odourless oil boiling at 269—270° under 30 mm. pressure, and shows no signs of solidifying when strongly cooled or kept for several months. It is insoluble in water, but dissolves readily in ether, benzene, or alcohol.

The molecular weight was determined by the freezing point method using benzene as solvent:

Wt. of ester.	Wt. of solvent.	Depression.	Mol. wt.
0·899 gram	20·83 grams	0·579°	365·2
1·4752 „	20·83 „	0·937	370·3

The molecular weight of $C_{18}H_{32}O_5(C_2H_5)_2$ is 386.

The *methyl* ester, $C_{18}H_{32}O_5(CH_3)_2$, was prepared by the action of methyl iodide on the dry silver salt. On analysis:

0·1498 gave 0·3666 CO_2 and 0·1436 H_2O. C = 66·74; H = 10·65.
$C_{20}H_{38}O_5$ requires C = 67·04; H = 10·61 per cent.

It is a colourless, oily liquid boiling at 258—259° under 30 mm. pressure and is insoluble in water, but dissolves readily in alcohol or ether.

Amides.—Henry (*Compt. rend.*, 1885, 100, 944) has shown that the diamides of the dibasic acids (succinic, adipic, &c.) are more easily prepared from the methyl than from the ethyl ester by the action of an aqueous solution of ammonia. Experiments made with the ethyl ester showed that this statement also applies to the acid $C_{18}H_{34}O_5$, and the amides were consequently prepared from the methyl ester. Four grams of the methyl ester and 25 c.c. of an aqueous solution of ammonia, saturated at 0°, were heated together in a sealed tube at 185° for 12 hours. At the end of this time, the whole of the ester had disappeared, and a small amount of solid was present, which was filtered off (filtrate = A), dried on a porous plate, and purified by recrystallisation from rectified spirit. On analysis:

0·1202 gave 8·9 c.c. moist nitrogen at 14° and 760 mm. N = 8·71.
$C_{18}H_{36}O_3N_2$ requires N = 8·54 per cent.

The *diamide* is insoluble in water, ether, chloroform, or light petroleum, but readily dissolves in boiling acetone or alcohol, from the latter of which it separates in aggregates of fine needles melting sharply at 141°. It is insoluble in an aqueous solution of potassium hydroxide. The yield was small, only 0·7 gram being obtained from 11 grams of methyl ester.

The Amic Acid.—The filtrate (A) from the diamide was diluted with water and acidified with dilute hydrochloric acid, when the oil which separated out immediately solidified. It was filtered off, dried on a porous plate, and purified by recrystallisation from dilute alcohol. On analysis :

0·1478 gave 0·3556 CO_2 and 0·1410 H_2O. C = 65·61 ; H = 10·60.
0·1428 „ 5·9 c.c. moist nitrogen at 20° and 767 mm. N = 4·76.
0·2406 „ 9·8 c.c. „ „ 17° „ 764 mm. N = 4·75.
$C_{18}H_{35}O_4N$ requires C = 65·65 ; H = 10·64 ; N = 4·26 per cent.

The *amic acid* crystallises from rectified spirit in aggregates of colourless needles melting at 136°. It is insoluble in water, ether, chloroform, or light petroleum, but dissolves slowly in a solution of potassium hydroxide in the cold and readily on warming. Its alcoholic solution is acid to litmus paper and gives a marked effervescence with a solution of sodium hydrogen carbonate in the cold.

Silver Salt of the Amic Acid.—The amic acid was dissolved in dilute alcohol, neutralised with ammonia and the warm solution of the ammonium salt poured into an excess of a solution of silver nitrate, when the silver salt separated out as a somewhat sticky, white precipitate, which soon became hard and granular. The whole was heated nearly to boiling, filtered, and the precipitate washed with water and alcohol, dried, and analysed :

0·1476 gave 0·0368 Ag. Ag = 24·93.
$C_{18}H_{34}O_4NAg$ requires Ag = 24·77 per cent.

Action of Acetic Anhydride on the Acid.—Ten grams of the acid and 40 grams of acetic anhydride were boiled together for 3 hours in a flask attached to a reflux condenser. The acid readily dissolved in the anhydride on heating. On distilling the liquid product under 90 mm. pressure, the excess of acetic anhydride passed over below 90°, and the last traces of this substance were removed by raising the temperature to 130° for a short time and passing a slow current of dry air through the liquid. The acetylated product was then allowed to remain over solid potassium hydroxide in a vacuum for 4 days and analysed. The analytical results indicate that the substance is the

monoacetylated anhydride, $C_{18}H_{31}O_4 \cdot CO \cdot CH_3$, and not the monoacetylated acid, $C_{18}H_{33}O_5 \cdot CO \cdot CH_3$.

0·1396 gave 0·3464 CO_2 and 0·1226 H_2O. C = 67·67; H = 9·75.
$C_{20}H_{34}O_5$ requires C = 67·79; H = 9·60 per cent.
$C_{20}H_{36}O_6$ „ C = 64·51; H = 9·67 „

2·1208 grams of the acetylated product were boiled for 5 hours with an excess of an alcoholic solution of potassium hydroxide. The alcohol was then evaporated off and the liquid acidified with dilute sulphuric acid and distilled with steam. The distillate required 50·17 c.c. of decinormal potassium hydroxide for neutralisation; the acetic acid from 1 gram of the acetylated product would therefore require 23·65 c.c.

In a second experiment, the acetylated product, after removal of the excess of acetic anhydride by distillation in a vacuum, was repeatedly boiled with water to remove the last traces of this impurity; it was then filtered at 100° and dried in a vacuum over potassium hydroxide and sulphuric acid for 5 days. 1·9954 grams of this product were hydrolysed in the manner just described. The distillate required 41·9 c.c. of decinormal potassium hydroxide for neutralisation, whence 1 gram of the acetyl derivative would require 21·0 c.c.

The calculated amount for 1 gram of the monoacetylated anhydride, $C_{20}H_{34}O_5$, is 28·24 c.c. and for 1 gram of the monoacetylated acid, $C_{20}H_{36}O_6$, 26·8 c.c.

These results are not in close agreement with the calculated values for the acetylated anhydride or acid, but they undoubtedly show that a monoacetylated derivative is formed by the action of acetic anhydride on the acid.

The oil left in the steam distillation flask solidified to a hard mass on cooling and after one recrystallisation from dilute alcohol melted at 110°, which shows that the original acid is obtained on hydrolysis of the acetylated product.

The *acetylated anhydride* is a very viscous, light yellow liquid, which shows no signs of solidification on long standing. It is readily soluble in alcohol or ether and dissolves slowly in aqueous potassium hydroxide.

Action of Acetyl Chloride on the Acid.—Five grams of the acid and 25 grams of acetyl chloride were boiled together for 1 hour in a flask attached to a reflux condenser, when the acid slowly dissolved. The product was treated in a similar manner to that obtained by the action of acetic anhydride. On analysis:

0·1810 gave 0·4446 CO_2 and 0·1570 H_2O. C = 67·00; H = 9·64.
$C_{20}H_{34}O_5$ requires C = 67·79; H = 9·60 per cent.

1·7238 grams of this acetylated compound were hydrolysed and treated in a similar manner to the product obtained by the action of acetic anhydride as described above. The distillate required 44·0 c.c. of decinormal potassium hydroxide for neutralisation; the acetic acid obtained from 1 gram would therefore require 25·5 c.c.

The monoacetylated anhydride obtained by the action of acetyl chloride possesses the same properties as that obtained by the action of acetic anhydride.

Product Soluble in Chloroform.

The chloroform extract of the mixed acids (see p. 1318) on evaporation, left 37 grams of a residue which became semi-solid on standing. It was subjected to steam distillation until the distillate was only faintly acid. From this distillate, ether extracted 4·5 grams of a liquid which had a strong odour of pelargonic acid and from this 1·8 grams boiling at 249—255° were obtained, and identified as pelargonic acid by analysis of the silver salt (Ag = 40·41 per cent.) and preparation of the zinc salt which melted at 130°.

Acid $C_{18}H_{34}O_5$.—The oil which remained in the distillation flask partially solidified on cooling, and after spreading on a porous plate, yielded 16 grams of a solid material, which was then fractionally recrystallised from dilute alcohol until a substance of constant melting point was obtained. The amount of pure substance thus isolated was small, only about 6 grams being obtained from 200 grams of dihydroxystearic acid. On analysis:

0·1072 gave 0·2838 CO_2 and 0·1094 H_2O. C = 72·20; H = 11·34.
0·0866 „ 0·2288 CO_2 „ 0·0888 H_2O. C = 72·06; H = 11·39.
$C_{18}H_{34}O_3$ requires C = 72·48; H = 11·41 per cent.

The acid is sparingly soluble in cold light petroleum, but dissolves readily on heating. It is very readily soluble in chloroform, ether, ethyl acetate, or acetone in the cold, or in hot alcohol, and separates out from dilute alcohol in small but well formed plates, melting at 78·5—79°, and resolidifying at 76·5—77°.

The *sodium* salt was prepared by neutralising the acid with a warm solution of pure sodium hydroxide. A small quantity of alcohol was added to the solution, when, on cooling, the sodium salt separated out. It was recrystallised from dilute alcohol, from which it separated in glistening leaflets, which were dried at 100° and analysed.

0·2064 gave 0·0458 Na_2SO_4. Na = 7·19.
$C_{18}H_{33}O_3Na$ requires Na = 7·19 per cent.

The sodium salt is sparingly soluble in cold water, but dissolves

readily on heating. It is sparingly soluble in alcohol and insoluble in acetone.

The following attempts were made to reconvert the acid $C_{18}H_{34}O_3$ into dihydroxystearic acid, but in all three cases it was recovered unchanged: (1) boiling the acid with a 2 per cent. solution of potassium hydroxide for 11 hours; (2) boiling the acid with 10 per cent. sulphuric acid for 12 hours; (3) heating 0·5 gram of the acid, 30 c.c. of water, and 2 grams of barium hydroxide in a sealed tube at 143° for 8 hours. The investigation of this acid is being continued.

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CXXXIX.—*Note on the Supposed Formation of an Oxide of Hydrogen higher than the Dioxide.*

By WILLIAM RAMSAY, F.R.S.

THE possible existence of a higher oxide of hydrogen than H_2O_2 was suggested by A. Bach (*Ber.*, 1900, **33**, 1506) on the ground that when hydrogen peroxide is diluted with sulphuric acid, and treated with permanganate, the amount of oxygen evolved is in all cases greater than would have been produced, reckoning from the amount of permanganate used. Now, as Armstrong has justly pointed out (Proc., 1900, **16**, 134), Bach has failed to take into account the persulphuric acid, proved by Lowry and West to be formed by mixing hydrogen peroxide with sulphuric acid. But neither Armstrong nor Lowry and West have disproved Bach's contention that a peroxide may possibly exist. The following account of some simple experiments will, I think, render Bach's contention untenable.

1. The amount of oxygen liberated on addition of hydrogen peroxide to a mixture of permanganate and sulphuric acid is considerably greater than if the permanganate be added to a mixture of hydrogen peroxide and sulphuric acid. Thus, 2·2 c.c. of a dilute solution of peroxide, added to excess of permanganate, acidified with dilute sulphuric acid, gave 43·49 c.c. and 43·76 c.c. of oxygen; on adding the permanganate to a mixture of sulphuric acid and peroxide, 33·47 c.c. and 33·59 c.c. of oxygen were collected.

2. Less permanganate is required if it be added to a mixture of hydrogen peroxide and sulphuric acid than if peroxide be added to a mixture of permanganate and sulphuric acid. For example:

2·2 c.c. of peroxide mixed with sulphuric acid required 20·1 c.c. of permanganate; on the other hand, 40 c.c. of permanganate mixed with sulphuric acid required 2·2 c.c. of peroxide. If, however, an acid, unattackable by permanganate, be substituted for sulphuric acid—and one which is incapable of a higher stage of oxidation—the percentage of hydrogen peroxide calculated from the permanganate taken is in substantial agreement with that calculated from the oxygen evolved, in whichever order the reagents are mixed. To illustrate this statement, the following figures, obtained by the use of acetic acid, may be adduced:

Ten c.c. of a dilute solution of hydrogen peroxide, mixed with acetic acid, required 12·3 c.c. of a solution of permanganate, containing 0·00669 gram $KMnO_4$ per c c. The peroxide solution, therefore, contains 0·0044 gram per c.c.

Ten c.c. of the same peroxide solution, mixed with 12·3 c.c. of permanganate containing acetic acid, gave 26·0 c.c. of oxygen, calculated to normal temperature and pressure. This corresponds to 0·0042 gram per c.c.

Another solution of permanganate was made, containing 0·00694 gram per c.c.; with this, the amount of available oxygen in 10 c.c. of a solution of peroxide was determined by addition of peroxide to a mixture of permanganate and sulphuric acid; it amounted to 0·0354 gram. Five experiments were then made, in which the peroxide was added to a mixture of permanganate with acetic acid; and five in which the permanganate was added to a mixture of peroxide and acetic acid; the oxygen was collected and measured in each case, and its weight calculated. The results are given in the following table:

	Peroxide added.	Difference per cent.		Permanganate added.	Difference per cent.
1.	0·0365	+3·71	1.	0·0351	−0·34
2.	0·0350	−0·89	2.	0·0350	−0·89
3.	0·0350	−0·89	3.	0·0349	−1·27
4.	0·0351	−0·72	4.	0·0349	−1·38
5.	0·0355	+0·42	5.	0·0354	+0·20

The small error is probably to be ascribed to the solubility of the liberated oxygen in the liquid.

One other experiment remains to be chronicled; Baeyer's statement, that neither persulphuric acid nor Caro's acid rapidly affects permanganate, was confirmed (*Ber.*, 1901, **34**, 853).

Bach's results are now explicable. Having added permanganate of known strength to a mixture of peroxide and sulphuric acid, he imagined that he had determined the strength of the peroxide solution. But, in actual fact, he had used too little permanganate, owing to the formation of persulphuric acid, and thus he reckoned the amount of peroxide as smaller than it really was. The oxygen collected on adding

the peroxide to the mixture of permanganate and sulphuric acid was therefore too great for the apparent weight of peroxide present in solution, and so he was led to imagine the existence of a peroxide of hydrogen containing more oxygen than the dioxide.

My thanks are due to Messrs. H. Tempany, W. J. St. J. Alton, A. O. Jones, and A. C. Carter for carrying out the experiments described in this note.

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CXL.—*The Electrolytic Reduction of Nitrourea.*

By G. W. F. HOLROYD.

THIELE AND LACHMAN (*Annalen*, 1895, **288**, 303) obtained evidence of the formation of nitrosourea as the primary reduction product of nitrourea. This nitroso-compound appears to be very unstable, being readily decomposed by mineral acids or acetic acid, and although rather more stable in alkaline solution, it decomposes, even in such a solution, at a little above 0°.

With the object of reducing the nitrosourea before it decomposes and so preparing semicarbazide from nitrourea, Thiele and Heuser (*ibid.*, 311) added, in small quantities at a time, a mixture of nitrourea and hydrochloric acid to a mixture of zinc dust and ice. Since the temperature must be kept at about 0°, this operation is very laborious. The semicarbazide was separated from solution in the form of the compound $[(CH_3)_2C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2]_2,ZnCl_2$; the yield of this compound obtained by the authors was 40 to 55 per cent. of the calculated amount.

The experiments described below were undertaken in order to see whether the conditions necessary for the reduction might not be obtained more easily by using the electric current. The result was to show that the reduction may be effected electrolytically with the expenditure of very little labour. An aqueous solution of ammonium chloride served, in the majority of experiments, as the electrolyte.

The following are the conditions which I found most favourable for the reduction. Ten grams of nitrourea, prepared according to Thiele and Lachman's directions (*loc. cit.*, 281), are placed in a jar, and 80 grams of commercial ammonium chloride and 300 grams of water are added. The cathode and anode each consist of a sheet of wrought iron, the area of one side of the portion of each of these which is immersed in the liquid is 70 sq. cm. The anode must be at least 3

mm. thick. A current of 2 amperes is passed during 20 hours. The cell is immersed in a large vessel of cold water. Since the resistance of such a cell, although it increases as the electrolysis proceeds, does not exceed more than about one ohm, a large number of such cells can easily be arranged in series, the anode of one cell being bent round so as to dip into the next and form the cathode of this second cell, and so on.

In experiment 15, several cells of double the size and with double the charge of nitrourea, ammonium chloride, and water were placed in series. The yield given in the table refers to one of these cells; the rest of the product obtained in this experiment was not recrystallised.

After interrupting the current, the contents of the cell are filtered at the pump, the precipitated ferrous hydroxide is washed twice with water, the turbid filtrate rendered clear by acidifying with hydrochloric acid, the liquid again filtered if necessary, and 10 grams of benzaldehyde are added for every 10 grams of nitrourea used, in order to separate out the semicarbazide. The mixture is shaken in a bottle for a few minutes, allowed to stand for an hour, and the precipitated benzylidenesemicarbazide is then filtered off and washed with water.

The benzylidenesemicarbazide so obtained may be directly converted into semicarbazide hydrochloride. According to Thiele and Stange (*Annalen*, 1894, **283**, 21), benzylidenesemicarbazide gives 89 per cent. of the theoretical yield of semicarbazide hydrochloride. If the benzylidenesemicarbazide is required in a state of purity, it may be recrystallised from commercial alcohol (methylated spirit). The reduction gave a yield of recrystallised benzylidenesemicarbazide equal to 60 per cent. of the theoretical yield. The crude product probably contains 66 per cent. of the calculated amount, for 1 gram of pure benzylidenesemicarbazide gave 0·9 gram when recrystallised in the same manner.

I found this the most economical method of preparing semicarbazide hydrochloride.

Subjoined is a table showing the results of electrolysis under various conditions of temperature, size of electrodes, and density of current.

In calculating the density of current, both sides of the cathode have been counted as area of the cathode, with the exception of those cases where the iron box was used and of experiment 17, where the electrodes were very close to one another.

For purposes of estimation, the semicarbazide was converted into the benzylidene derivative.

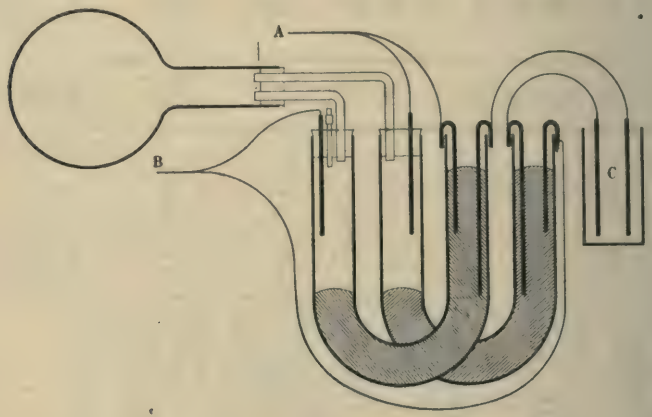
0·1160 of the product in experiment 15 gave 26·1 c.c. of nitrogen at 17° and 758 mm. N = 26·05.

$C_8H_9ON_3$ requires N = 25·76 per cent.

Number of experiment.	Nature of electrolyte.	Nature and size of electrodes.	Amperes.	Density of current in amperes per sq. cm. of cathode.	Temperature.	Per cent. of current effective in producing semicarbazide.	Hours during which current was passed.	Grams of nitrourea used.	Grams of recrystallised benzylidenesemicarbazide.	Per cent. of theoretical yield.
1	24 grams of ammonium chloride, 90 grams of water.	Cathode, a wrought iron box containing the electrolyte, 115 sq. cm. in contact with liquid; anode, 70 sq. cm. wrought iron.	1	0·0087	20°	12·9	6	1	0·79	50·9
2	,,	Cathode same as in 1, with iron plate attached; total area, 286 sq. cm.; anode as in 1.	1	0·0035	,,	12·1	,,	,,	0·74	47·7
3	,,	Cathode and anode as in 1.	1	0·0087	,,	19·0	4	,,	0·80	51·6
4	,,	,,	1	,,	−5	12·7	6	,,	0·78	50·3
5	,,	Cathode as in 1; anode, 360 sq. cm. wrought iron.	1	,,	20	20·3	4	,,	0·83	53·5
6	,,	Cathode, a strip of wrought iron 15 sq. cm.; anode as in 1.	1	0·066	,,	15·7	6	,,	0·96	61·9
7	,,	Cathode, a strip of wrought iron 7 sq. cm.; anode as in 1.	1	0·143	,,	18·4	4	,,	0·75	48·4
8	,,	,,	1	,,	,,	16·03	6	,,	0·98	63·2
9	,,	Cathode and anode as in 1.	1	0·066	,,	29·9	2	,,	0·61	39·35
10	8 grams of ammonium chloride, 30 grams of water.	,,	1	,,	,,	22·5	4	,,	0·92	59·35

11	24 grams of ammonium chloride, 90 grams of water.	Cathode, a strip of wrought iron 30 sq. cm.; anode, 70 sq. cm. wrought iron.	2	,,	,,	16·3	3	,,	1·0	64·51
12	,,	Cathode and anode as in 6.	0·3	0·02	,,	24	15	,,	1·1	70·90
13	80 grams of ammonium chloride, 300 grams of water.	Cathode, a wrought iron plate 150 sq. cm.; anode, ditto.	2	0·013	,,	22·9	20	10	9·34	60·25
14	,,	,,	2	,,	,,	18·1	25	,,	9·24	59·61
15	150 grams of ammonium chloride, 600 grams of water.	Cathode, a wrought iron plate 300 sq. cm.; anode, ditto.	3	0·01	,,	21·1	27	20	17·46	56·32
16	25 grams of ammonium chloride, 73 of water, 22 of ammonia of sp. gr. 0·880.	The electrodes were sheets of zinc; 70 sq. cm. of each were in contact with the liquid.	4	0·114	,,	7·7	20	10		40·58
17	8 grams of ammonium chloride, 25 of water, 5 of ammonia of sp. gr. 0·880 (the nitrourea was added gradually.)	The electrodes were discs of zinc placed one above the other, the area of one side of each was 50 sq. cm.	5	0·1	,,	13·6	1½	1	0·928	59·9
18	50 grams of sodium chloride, 150 of water in outer cell; same solution in a porous inner cell.	Cathode, platinum foil, 72 sq. cm. in outer cell; anode, carbon in inner cell.	1·9	0·026	−2	17·4	8	5	2·69	34·7
19	200 grams of 18 per cent. hydrochloric acid in outer cell; hydrochloric acid of same strength in inner porous cell.	Cathode and anode as in 18.	1·9	,,	−5	15·4	,,	,,	2·39	30·8
20	200 grams of 18 per cent. hydrochloric acid in outer cell; hydrochloric acid of same strength in inner cell	,,	1·9	,,	,,	6·4	,,	2	0·99	32·1

In experiment 16, the electrolysis was interrupted after 10 hours and begun again on the following day; the nitrourea was added in portions of 1 gram at intervals of 2 hours. When electrolysis was at an end, the solution was filtered and 5 grams of acetone were added, a crystalline deposit of the compound $[(CH_3)_2C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2]_2,ZnCl_2$ was formed. This precipitate was filtered off after some hours, and dried on a porous plate; it then weighed 5·95 grams. One gram of this precipitate was dissolved in water, 1 gram of benzaldehyde added, and the solution heated to boiling; the benzylidenesemicarbazide thus formed was collected and recrystallised from alcohol; it then weighed 0·73 gram. The 5·95 grams of zinc compound would, therefore, have given 4·34 grams of recrystallised benzylidenesemicarbazide; this corresponds to a yield of 28 per cent. of the theoretical. 1·95 grams of recrystallised benzylidenesemicarbazide were obtained from the filtrate



from the zinc compound; this corresponds to a yield of 12·58 per cent. A total yield of 40·58 per cent. of the theoretical was, therefore, obtained in this experiment.

In all the other experiments, the semicarbazide was precipitated directly as the benzylidene derivative.

Experiment 17 shows that a good yield may be obtained when zinc poles are used, if the nitrourea be added very gradually.

In the case of experiments 16 and 17, where zinc poles were used, an alternating current was employed to prevent the formation of a bridge of zinc from pole to pole.

A little piece of apparatus which I found very useful for alternating a direct current, depends on an observation made some years ago by Mr. A. G. Vernon Harcourt. If a vessel containing air be heated and connected, by means of glass tubing, with a U-tube containing mercury,

and an oscillatory motion be imparted to the mercury, this motion is maintained so long as the vessel containing air is heated.

I proposed to use this arrangement as a source of energy to work an ordinary rocking alternator. I am, however, indebted to Mr. D. H. Nagel, of Trinity College, for the suggestion that I should use the oscillating mercury in the U-tube directly for making and breaking contact. This I did in the following manner.

I placed a flask of 250 c.c. capacity in a horizontal position above an argand burner and connected it, by means of a doubly-bored cork and bent glass tubes, with two U-tubes half-filled with mercury. By imparting simultaneously to the mercury in both U-tubes an oscillatory motion (by depressing the mercury in the outer limbs by two corks fixed on the ends of little rods), I obtained the necessary movement of the mercury. This movement is maintained so long as the flask is heated. By the arrangement of wires shown in the figure (p. 1330), a current may be sent first in one direction and then in the opposite direction through an electrolytic cell. The wires which come in contact with the mercury should be of iron.

Thiele and Lachman remark with respect to primary nitrosoamines: "These nitrosoamines are generally very unstable bodies, and it is owing to their production that the reduction of primary nitroamines generally gives such unsatisfactory yields" (*loc. cit.*).

A method similar to the above may probably be applied with advantage to the reduction of other nitroamines and nitrosoamines. This I hope to test in the near future.

I wish to express my thanks to Mr. D. H. Nagel, of Trinity College, Oxford, for kindly allowing me to carry out these experiments in the Laboratory of Balliol and Trinity Colleges.

CHRIST CHURCH, OXFORD.

CXLI.—*The Constitution of Pilocarpine. Part III.*

By HOOPER ALBERT DICKINSON JOWETT.

IN previous papers (Trans., 1900, **77**, 851, this vol., 580), it was shown that by the oxidation of *iso*pilocarpine with permanganate a small quantity of acetic acid is formed together with a crystalline lactonic acid, $C_7H_{10}O_4$, to which the name *pilopic acid* was assigned.

The present paper deals with a fuller examination of the products of oxidation of the alkaloid and with the constitution of pilopic acid.

By the oxidation of larger quantities of *iso*pilocarpine, it has been found that in addition to the acids above mentioned, small quantities of *propionic acid* and of a new acid, *homopilopic acid*, $C_8H_{12}O_4$, homologous with pilopic acid, are also obtained.

Although the correctness of the formula for pilopic acid has been questioned by Pinner and Kohlhammer (*Ber.*, 1900, **33**, 1424, 2357; 1901, **34**, 727), its accuracy has been confirmed, not only by analyses of the ethyl and methyl esters and of the crystalline acid and various derivatives, but particularly by the determination of the molecular weight of the methyl ester. The pure crystalline acid has been characterised and the anilide and the strychnine salt prepared in crystalline form and examined. The lactonic nature of pilopic acid has been proved by the preparation of the barium and silver salts and of the crystalline diamide of the corresponding hydroxy-acid, the behaviour of the acid in the last case recalling that of *iso*hexolactone, which with ammonia yields γ-hydroxy*iso*hexoamide. The reaction may be expressed by the following equation:

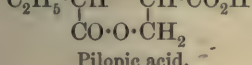
$$CO_2Et\cdot C_5H_9\!<\!\begin{matrix}CO\\ |\\ O\end{matrix} + 2NH_3 = OH\cdot C_5H_9(CO\cdot NH_2)_2 + Et\cdot OH.$$

Homopilopic acid has not been crystallised, but the diamide of the hydroxy-acid has been obtained in well-defined crystals and the lactonic nature of the acid proved by the preparation of the barium salt of the hydroxy-acid. It is also shown that there are grounds for regarding Pinner and Kohlhammer's piluvic acid as a mixture of pilopic and homopilopic acids.

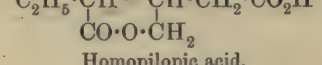
In a previous paper (Trans., 1900, **77**, 858), it was shown that from ethyl pilopate, by treatment with phosphorus pentabromide, &c., a small quantity of *iso*butyric acid was obtained. Repetition of this experiment with a larger quantity of material and the isolation and examination of the intermediate products of the reaction have shown that the quantity of *iso*butyric acid formed is very small and is produced by secondary reactions. As the constitutional formula previously proposed for pilopic acid was founded on the production of *iso*butyric acid as the main product of the reaction, the deductions are invalid and the formula must therefore be abandoned. By fusion of pilopic acid with potassium hydroxide at a high temperature, normal butyric acid is formed, whilst at a low temperature most of the acid is not attacked, but a small portion is converted into the isomeric unsaturated acid.

When homopilopic acid is fused with potassium hydroxide at a medium temperature, *α-ethyltricarballylic* acid is produced, and this acid has been identified beyond question by the formation of certain characteristic derivatives (see following paper).

Finally, it is shown that in all probability the constitution of pilopic and homopilopic acids may be represented by the following formulæ:



Pilopic acid.



Homopilopic acid.

Experimental.

Oxidation of iso*Pilocarpine and formation of Propionic Acid.*

About 1 kilo. of *iso*pilocarpine nitrate was oxidised with permanganate in the manner previously described, with this modification—that all the volatile acids formed were removed by steam distillation of the acid liquid previous to concentration and subsequent extraction with alcohol. The aqueous solution of the volatile acids, which was free from any rancid odour, was neutralised and evaporated to a low bulk, acidified with sulphuric acid, and extracted with ether. After removal of the ether by evaporation, the residue, which smelt strongly of acetic acid, was distilled. The first fraction, which came over below 120°, consisted chiefly of acetic acid and was not further examined. The remainder of the liquid distilled completely between 120° and 140°, the greater portion coming over at 136°. The distillate was converted into the crystalline barium salt, from which the silver salt was obtained in three fractions by precipitation with aqueous silver nitrate. Each fraction was analysed with the following results:

Fraction 1.	0·2706 gave	0·1616 Ag.	Ag = 59·7.
,, 2.	0·1116 ,,	0·0666 Ag.	Ag = 59·7.
,, 3.	0·061 ,,	0·0366 Ag.	Ag = 60·0.

$C_3H_5O_2Ag$ requires Ag = 59·7 per cent.

In order to complete the proof of the identity of the acid, it was converted into the anilide, which melted at 103°, and on analysis furnished the following result:

0·1542 gave 13·6 c.c. nitrogen at 15° and 753 mm. N = 10·0.

$C_9H_{11}ON$ requires N = 9·4 per cent.

The only volatile acids formed during the oxidation of *iso*pilocarpine with permanganate are therefore *acetic* and *propionic* acids.

Fractional Distillation of the Ethyl Esters.

In order to determine the composition of the ethyl ester obtained by the oxidation of *iso*pilocarpine, it was submitted to careful fractionation.

One hundred and thirty grams of the crude ester were twice

refractionated under 10 mm. pressure and the following fractions obtained.

Below 160°.....	20 grams	170—175°.....	22 grams
160—165°.....	10 „	Above 175°.....	12 „
165—170°.....	52 „		

The fractionation in a vacuum was found to be unsatisfactory, as any slight variation in the pressure, which is almost unavoidable, affected the distilling point to a considerable extent.

An attempt was made to fractionate the ester under the ordinary pressure, using the rod and disc fractionating apparatus (Young, Trans., 1899, **75**, 689) and a metal bath. This method, however, was only partially successful, owing to the risk of fracture of the flask by the high boiling liquid and to the loss of valuable material by decomposition in each distillation. If a small quantity, for example, 20 grams, of the ester be rapidly distilled from an ordinary distilling flask, it appears to boil quite constantly at 299° with very little decomposition, and a similar result is obtained by distilling it in a vacuum. As the result of three fractionations, the whole of the liquid was separated into three main fractions, which were analysed with the following results:

Fraction 1. B. p. 290—300° (or 164—166° under 10 mm. pressure).
0·2126 gave 0·4544 CO_2 and 0·1446 H_2O. C = 58·3; H = 7·6.
Fraction 2. B. p. 300—310°.
0·2102 gave 0·4544 CO_2 and 0·152 H_2O. C = 59·0; H = 8·0.
Fraction 3. B. p. 310—312° (or 210° under 10 mm. pressure).
0·1538 gave 0·338 CO_2 and 0·1126 H_2O. C = 59·9; H = 8·1.

$C_9H_{14}O_4$ requires C = 58·1; H = 7·5 per cent.
$C_{10}H_{16}O_4$ „ C = 60·0; H = 8·0 „
$C_{12}H_{20}O_5$* „ C = 59·0; H = 8·2 „

The greater portion of the ester was contained in fractions 1 and 2.

From these results, it would appear that two homologous esters are present, the first and third fractions each consisting of an almost pure ester and the second fraction being a mixture. This will account for the high figures persistently obtained for the carbon, as it is almost impossible to procure the lower fraction quite free from the higher homologue.

The first fraction on hydrolysis readily yields the crystalline pilopic acid, but the second and third fractions only yield an oil which could not be crystallised.

By distillation of the second fraction in a vacuum, it was possible to

* Pinner and Kohlhammer's formula.

effect a separation into three fractions, similar to those previously described, thus proving it to be a mixture of the two homologous esters.

Pilopic Acid, $C_7H_{10}O_4$.

This acid, which was crystallised with considerable difficulty, was prepared as follows. The ethyl ester boiling at 290—300° was hydrolysed either by aqueous potassium hydroxide or by 40 per cent. sulphuric acid, and the acid liquid saturated with ammonium sulphate and extracted by ether. The ethereal solution of the acid was next extracted with sodium carbonate solution, and the alkaline liquid subsequently acidified with sulphuric acid, saturated with ammonium sulphate, and extracted by ether. The ethereal extract was washed with water, dried over calcium chloride, and distilled. The syrupy residue, after standing for several days in a vacuous desiccator over sulphuric acid, with frequent stirring, became pasty and almost solid. It was spread on a porous tile, and the crystalline crust thus obtained recrystallised several times from hot benzene. After several recrystallisations, it separated in silky plates melting constantly at 104° (corr.). The acid can also be crystallised from water, in which, however, it is very soluble. On analysis:

0·09 gave 0·1748 CO_2 and 0·0526 H_2O. C = 53·0; H = 6·5.
0·1528 „ 0·297 CO_2 „ 0·0904 H_2O. C = 53·0; H = 6·57.
$C_7H_{10}O_4$ requires C = 53·2; H = 6·3 per cent.

The acid is dextrorotatory, and a determination of the specific rotation in aqueous solution gave the following result:

$\alpha_D^{15°} = +1·2°$; $l = 1$ dcm.; $c = 3·324$; $[\alpha]_D^{15°} = +36·1°$.

When excess of alkali is added to the acid solution, the specific rotation diminishes, a property also shown by pilocarpine and *iso*pilocarpine. A determination of the specific rotation in alkaline solution gave the following result:

$\alpha_D^{17°} = +0·3°$; $l = 1$ dcm.; $c = 9·5$; $[\alpha]_D^{17°} = +3·2°$.

The *methyl ester*, prepared in the usual way by means of sulphuric acid and methyl alcohol, is a colourless liquid boiling at 155—160° under 10 mm., and at 275° under 757 mm. pressure. On analysis:

0·1534 gave 0·315 CO_2 and 0·099 H_2O. C = 56·0; H = 7·2.
$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

In order to prove conclusively the correctness of the formula $C_7H_{10}O_4$, proposed for pilopic acid, the molecular weight of the methyl ester was determined. Although the percentages of carbon and hydrogen required for the formulæ proposed by the author and by

Pinner and Kohlhammer are not very dissimilar, there is a considerable difference in the molecular weights of the corresponding ester. The molecular weight was determined by the depression of the freezing point of benzene and of glacial acetic acid.

Solvent.	Wt. of ester.	Wt. of solvent.	Depression.	Mol. wt.
Benzene	0·3322	13·98	0·65°	179
Glacial acetic acid	0·3964	15·762	0·59	166

Molecular weight of $C_8H_{12}O_4$ = 172

" " $C_{10}H_{16}O_5$ = 216 (P. and K. formula)

These results, in addition to the analytical data recorded in this paper, conclusively prove the correctness of the formula $C_7H_{10}O_4$ previously ascribed to pilopic acid.

The *barium* salt of pilopic acid was prepared by digesting an aqueous solution of the acid with excess of barium carbonate, filtering, evaporating the filtrate to a low bulk, and precipitating with alcohol. The microcrystalline salt, dried at 120°, was analysed with the following result:

0·1406 gave 0·0722 $BaSO_4$. Ba = 30·2

$(C_7H_9O_4)_2Ba$ requires Ba = 30·4 per cent.

The *anilide*, $C_7H_9O{\cdot}NH{\cdot}C_6H_5$, was prepared by boiling the acid with three times its weight of aniline in a reflux apparatus for 24 hours. The liquid was poured into excess of dilute hydrochloric acid and the acid liquid extracted with ether. The ethereal extract was washed four times with dilute acid, finally with water, and dried over calcium chloride. After removal of the ether by distillation, the residue was placed in a vacuous desiccator over sulphuric acid and frequently stirred. In a short time, the oil became almost solid; the mass was spread on a porous tile and the dry powder then recrystallised from hot ether until of constant melting point. It was thus obtained in white, flat, pearly plates melting sharply at 110° (corr.). On analysis:

0·1124 gave 6·4 c.c. nitrogen at 22° and 764 mm. N = 6·3.

$C_{13}H_{15}O_3N$ requires N = 6·0 per cent.

The *strychnine* salt was prepared by boiling the aqueous solution of the acid with excess of strychnine and filtering. The filtrate was then evaporated in a vacuous desiccator over sulphuric acid and a very hygroscopic crystalline mass obtained, which was dissolved in a little hot alcohol. On standing, after the addition of ether, a quantity of strychnine separated, which was removed, and more ether added to the mother liquor. After long standing in a stoppered bottle, rosettes of crystals separated. These were dried and found to be very soluble in

water or alcohol and to melt at 120° (corr.); the aqueous solution was acid to litmus. On analysis:

0·186 gave 7·6 nitrogen at 22° and 764 mm. N = 4·5.
0·1606 „ 0·0832 anhydrous strychnine = 51·8.
$C_{21}H_{22}O_2N_2(C_7H_{10}O_4)_2$ requires N = 4·3; strychnine = 51·4 per cent.

This was therefore the acid salt of strychnine, formed by the separation of strychnine from the normal salt which was apparently first produced.

The *diamide* of the *hydroxy-acid* was prepared by mixing equal volumes of the methyl or ethyl ester of pilopic acid and strong aqueous ammonia. After standing for some hours with frequent shaking, the oil disappeared and the liquid solidified to a mass of crystals which was drained on a porous tile and recrystallised from hot alcohol until of constant melting point. The amide was sparingly soluble in cold water or alcohol, fairly so in hot water or alcohol, and almost insoluble in ether, benzene, or chloroform. The crystals melted at 160° (corr.), and on analysis yielded the following results:

0·0934 gave 0·167 CO_2 and 0·069 H_2O. C = 48·7; H = 8·2.
0·1206 „ 17·0 c.c. nitrogen at 14° and 764 mm. N = 16·4.
$C_7H_{14}O_3N_2$ requires C = 48·3; H = 8·1; N = 16·1 per cent.

Lactonic character of Pilopic Acid.—The correctness of the formula for pilopic acid having been demonstrated, experiments were next undertaken to obtain further proof of its lactonic character. Two grams of the acid were boiled with excess of baryta water for an hour, the solution saturated with carbon dioxide, and filtered. The filtrate was evaporated to a low bulk, acidified with the requisite quantity of sulphuric acid, and extracted with ether. The ethereal solution was washed with water, the ether spontaneously evaporated, and the residue placed overnight in a desiccator over sulphuric acid. It was then titrated with normal alkali, using phenolphthalein as indicator, with the following results:

0·52 required in the cold, 3·4 c.c. for neutralisation, and, when boiled with excess of alkali and titrated back with acid, 6·5 c.c.; this amount of an acid, $C_7H_{10}O_4$, requires 3·3 c.c. and 6·6 c.c. respectively. The substance was therefore the lactonic acid.

The *barium* salt of the *hydroxy-acid* was prepared by adding alcohol to a concentrated aqueous solution of the salt, prepared as just described. The precipitate was filtered off and dried on a porous tile. On analysis, the air-dried salt yielded the following result:

0·1404 gave 0·0982 $BaSO_4$. Ba = 41·1.
0·258 at 150° lost 0·0112 H_2O. H_2O = 4·4.
$C_7H_{10}O_5Ba,H_2O$ requires Ba = 41·6; H_2O = 5·5 per cent.

The specific rotation of the barium salt was determined in aqueous solution with the following result.

$$\alpha_D^{15°} = +0{\cdot}216°;\ l = 1 \text{ dcm.};\ c = 3{\cdot}512;\ [\alpha]_D^{15°} = +6{\cdot}1°.$$

The *silver* salt of the *hydroxy-acid*, prepared from the barium salt by interaction with silver nitrate, was a gelatinous precipitate, which, after drying on a porous tile, yielded, on analysis, the following result:

0·256 gave 0·1404 Ag. Ag = 55·0.

$C_7H_{10}O_5Ag_2$ requires Ag = 55·4 per cent.

Action of Ammonia on the Ethyl Esters (Middle Fraction).

The middle fraction of the ethyl ester obtained from the oxidation of *iso*pilocarpine (p. 1334) was shaken with an equal volume of strong ammonia, and a crystalline amide obtained melting at 151°. This was recrystallised many times from hot alcohol and from water, and a small quantity of an amide melting at 200° separated. As this proved to be identical with the amide obtained from the third fraction of the ester, it was set aside. The crystals from the mother liquors were recrystallised several times from alcohol and from water, and a product obtained melting at 161°, but analysis showed that it was not pure, so that it was not possible to separate the homologous amides completely by this method. In spite of all attempts to separate this middle fraction into its constituents, it could not be purified further than into two portions, one chiefly ethyl pilopate, and the other containing only a small quantity of this ester.

Homopilopic Acid, $C_8H_{12}O_4$.

The third fraction of the ethyl esters obtained by the oxidation of *iso*pilocarpine (p. 1334) gave, on analysis, results agreeing with those required for an ester of the formula $C_{10}H_{16}O_4$. On treatment with ammonia, a crystalline amide was obtained which melted at 199°. This *amide*, together with the portion melting at 200° from the second fraction of the ester, was recrystallised from water and from hot alcohol until of constant melting point. It was readily crystallised from hot water, and separated in well-defined prisms melting sharply at 208° (corr.) On analysis:

0·158 gave 0·2938 CO_2 and 0·1246 H_2O. C = 50·7; H = 8·7.

0·1172 ,, 15 c.c. nitrogen at 20° and 769 mm. N = 14·6.

$C_8H_{16}O_3N_2$ requires C = 51·1; H = 8·5; N = 14·9 per cent.

As in the case of the pilopic ester, the diamide of the hydroxy-acid is formed in this reaction.

The *acid*, for which the name *homopilopic acid* is proposed, was obtained from the pure amide by heating with 20 per cent. hydrochloric acid in a sealed tube at 120°. The acid was extracted with ether, the ethereal solution washed with water, dried over calcium chloride, and distilled. The residual oil, after remaining in a vacuous desiccator over sulphuric acid for some days, showed no signs of crystallisation, and was therefore distilled in a vacuum. It boiled at 235—237° under 20 mm. pressure. On analysis:

0·141 gave 0·2864 CO_2 and 0·092 H_2O. C = 55·4; H = 7·2.
$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

The acid is dextrorotatory, and a determination of its specific rotation in aqueous solution gave the following result:

$\alpha_D^{21°} = +1·6°$; $l = 1$ dcm.; $c = 3·524$; $[\alpha]_D^{21°} = +45·4°$.

With excess of alkali, the specific rotation is diminished:

$\alpha_D^{21°} = +0·16°$; $l = 1$ dcm.; $c = 2·82$; $[\alpha]_D^{21°} = +5·9°$.

The acid was titrated with decinormal alkali, using phenolphthalein as indicator, with the following results:

0·185 required in the cold, 10·5 c.c. for neutralisation, and, when boiled with excess of alkali and titrated back with acid, 21·4 c.c.; this amount of an acid, $C_8H_{12}O_4$, requires 10·75 c.c. and 21·5 c.c. respectively.

The barium salts of the lactonic and hydroxy-acids were prepared in a manner similar to the corresponding salts of pilopic acid.

The *barium* salt of the *lactonic acid* is a very hygroscopic powder, which, dried at 150°, yielded the following result on analysis:

0·1614 gave 0·079 $BaSO_4$. Ba = 28·8.
$(C_8H_{11}O_4)_2Ba$ requires Ba = 28·6 per cent.

The *barium* salt of the *hydroxy-acid*, which is microcrystalline and stable in the air, contains 1 mol. of water of crystallisation. On analysis of the air-dried salt:

0·6094 at 150° lost 0·0314 H_2O. $H_2O = 5·1$.
0·3542 gave 0·2414 $BaSO_4$. Ba = 40·1.
$C_8H_{12}O_5Ba,H_2O$ requires Ba = 40·0; $H_2O = 5·3$ per cent.

Pinner and Kohlhammer's Piluvic Acid.

It having been proved that pilopic acid has not the same formula as piluvic acid, the question arises whether homopilopic and piluvic acids may not be identical. Although it is not possible to decide this question definitely, inasmuch as no physical constants have been recorded for piluvic acid by means of which it may be identified, and as no proof

has yet been adduced that the acid and its derivatives were pure products, yet there are a number of facts which suggest the possibility of the identity of these acids, or, at any rate, that piluvic acid consisted largely of homopilopic acid.

Forty grams of *iso*pilocarpine were oxidised with 127 grams of permanganate in the cold, and the ethyl ester isolated by the usual method. On distillation under 20 mm. pressure, three fractions were obtained boiling at 160—170°, 170—190°, and 190—240° respectively. The lowest fraction, distilled under 760 mm. pressure, gave a liquid boiling at 295°, which was analysed with the following results:

0·1996 gave 0·4126 CO_2 and 0·1308 H_2O. C = 57·6; H = 7·3.
$C_9H_{14}O_4$ requires C = 58·1; H = 7·5 per cent.

The liquid was therefore ethyl pilopate, so that, under the conditions of this oxidation, pilopic acid was formed.

Experiments were made, using larger quantities of permanganate than previously employed, in order to obtain pilopic acid free from homopilopic acid, but this purpose was not accomplished, although the amount of volatile acids appeared to increase. It is more probable, therefore, that in the oxidation of *iso*pilocarpine the molecule is attacked at two points, namely, at contiguous carbon atoms, with the formation of pilopic and homopilopic acids, rather than that homopilopic acid is first produced and then oxidised to pilopic acid. It is of course possible that both factors come into play when a large excess of permanganate is used. Pinner and Kohlhammer may therefore have been dealing with a mixture of pilopic and homopilopic acids, and their analytical results are in harmony with such a suggestion. Moreover, there is an experiment recorded by them which supports this view, namely, that in which an attempt was made to purify the amyl ester by distillation. In this case, the analytical results did not agree with any formula, and the authors admit the ester was impure; it was, however, prepared from the barium salt of the acid by a simple reaction, such as would lead to the formation of a product requiring only a single fractionation to obtain it in a state of purity. The fact that the ester was not pure throws doubt on the purity of the barium salt, although it is on the analysis of this salt, and of the acid derived from it, that the proof of the formula, $C_8H_{12}O_5$, given by Pinner and Kohlhammer for piluvic acid is partly based.

Experiments on the Constitution of Pilopic and Homopilopic Acids.

For the purposes of these experiments, the syrupy acid was used, analysis having shown that only a small proportion of homopilopic acid was present. Twenty-four grams of ethyl pilopate were treated with

phosphorus pentabromide, as already described (Trans., 1900, 77, 858), and 20 grams of an ester boiling at 180—190° under 10 mm. pressure obtained. This, when treated with diethylaniline, yielded 13 grams of a product which, when fractionated, first in a vacuum and then under the ordinary pressure, could be divided into two fractions: (1) 270—290°, a limpid oil; (2) 290—300°, a thicker oil, showing a tendency to deposit a waxy substance.

The first fraction proved to be ethyl pilopate, and by hydrolysis the crystalline pilopic acid was obtained from it. On analysis of the ester:

0·0946 gave 0·2016 CO_2 and 0·0672 H_2O. C = 58·1; H = 7·8.
$C_9H_{14}O_4$ requires C = 58·1; H = 7·5 per cent.

The second fraction, on analysis, yielded the following result:

0·1014 gave 0·2262 CO_2 and 0·0714 H_2O. C = 60·8; H = 7·8.
$C_{11}H_{18}O_4$ requires C = 61·7; H = 8·4 per cent.

It was not therefore the expected diethyl ester of the unsaturated acid. On hydrolysis, a syrupy acid was obtained which did not crystallise even when left in a vacuum over sulphuric acid at 0° for several days.

This acid yielded an amorphous silver salt containing 53·1 per cent. Ag ($C_7H_8O_4Ag_2$ requires Ag = 58·1 per cent.). It was oxidised with permanganate at 0°, and an oily acid with a rancid odour was isolated from the products of the reaction. The silver salt prepared from this acid contained 51·4 per cent. Ag, but the quantity obtained was too small to purify, and as it was evident that this amount of acid did not represent the main reaction, the experiment was abandoned.

Action of Hydriodic Acid on Pilopic Acid.—The acid was heated with three times its weight of fuming hydriodic acid in a reflux apparatus for several hours, but the pilopic acid was recovered unchanged. When heated in a sealed tube at 180°, no crystalline product was obtained, but only a small quantity of an oil having the odour of petroleum.

A quantity of the acid was heated to 210° in a sulphuric acid bath, but no change took place, no gas or water being given off.

Fusion of Pilopic Acid with Potassium Hydroxide.

Fusion at a High Temperature.—Five grams of the syrupy acid were mixed with 25 grams of potassium hydroxide and a few drops of water, and the mixture fused for a short time. The fused mass was dissolved in water, acidified with sulphuric acid, and distilled with steam. The distillate, which had a rancid smell, was extracted with ether, the ethereal solution dried over calcium chloride, and distilled.

The residue distilled completely at 110—160°, and the distillate was miscible with water. The barium salt was prepared and analysed:

0·2672 gave 0·2014 $BaSO_4$. Ba = 44·3.
$(C_4H_7O_2)_2Ba$ requires Ba = 44·1 per cent.

The calcium salt was also prepared, and obtained as white, pearly plates, which were dried on a porous tile, and, on analysis, yielded the following result:

0·127, air-dried, lost 0·0112 H_2O at 150°. H_2O = 8·8.
$(C_4H_7O_2)_2Ca,H_2O$ requires H_2O = 7·8 per cent.

Calcium *iso*butyrate crystallises with 4 mols. of water of crystallisation. Further proof of the identity of this salt with calcium *n*-butyrate was afforded by making a saturated aqueous solution of the salt at 0°, and placing the solution in warm water, when crystals separated which redissolved on cooling to 0°.

The silver salt was prepared, and, after recrystallising once from hot water, furnished the following result on analysis:

0·136 gave 0·0752 Ag. Ag = 55·3.
$C_4H_7O_2Ag$ requires Ag = 55·4 per cent.

The volatile acid formed is therefore *normal butyric acid*. No other acid could be isolated from the residue left after distillation.

Fusion at a Low Temperature.—Ten grams of acid were fused with 30 grams of potassium hydroxide and 5 c.c. of water, and kept gently simmering for some time. The fused mass was dissolved in water, acidified with sulphuric acid, and distilled with steam, but no volatile acid was obtained. The acid liquid was extracted with ether, the ethereal solution washed with water, dried over calcium chloride, and distilled. The residue weighed 6 grams, and on standing in a vacuum for some time, deposited a small quantity of crystals, which were separated, and drained on a porous tile. The non-crystalline residue was found to be unchanged pilopic acid. The residual liquid, after extraction with ether, was neutralised, evaporated to dryness, and extracted with alcohol. The alcohol was removed by distillation, the residue dissolved in a little water, and precipitated with lead acetate. The acid, regenerated from the lead salt by means of sulphuretted hydrogen, gave crystals mixed with unchanged pilopic acid, and when recrystallised from hot water came out in scales. When pure, it melted at 190° (corr.), losing water, and forming, apparently, the anhydride. On analysis:

0·0258 gave 0·05 CO_2 and 0·016 H_2O. C = 52·8; H = 6·9.
$C_7H_{10}O_4$ requires C = 53·2; H = 6·3 per cent.

The acid was almost insoluble in ether, and sparingly soluble in cold water; it decolorised permanganate solution.

The silver salt was obtained as a granular precipitate on adding silver nitrate to a solution of the ammonium salt of the acid. After washing, it was dried on a porous tile and analysed, with the following result:

0·116 gave 0·0674 Ag, 0·094 CO_2, and 0·0238 H_2O. Ag = 58·1; C = 22·1; H = 2·3.

$C_7H_8O_4Ag_2$ requires Ag = 58·1; C = 22·6; H = 2·1 per cent.

From a consideration of the properties of this acid, it would appear probable that it is an unsaturated acid closely allied to ethylitaconic acid, and that it is produced from the lactonic acid by a similar reaction to that generally brought about by sodium ethoxide.

By fusion at a low temperature, therefore, a small quantity of the isomeric unsaturated acid is formed, but the greater portion of the lactonic acid is recovered unchanged.

Fusion of Homopilopic Acid with Potassium Hydroxide and Formation of α-Ethyltricarballylic Acid.

A preliminary experiment having shown that a crystalline acid is formed by the fusion of homopilopic acid with potassium hydroxide at a moderate temperature, the whole of the syrupy homopilopic acid at disposal was fused with three times its weight of the alkali and a little water for half an hour; the mass was then dissolved in water, acidified with sulphuric acid, and distilled with steam. Only a trace of a volatile acid was obtained.

The acid liquid remaining after distillation was extracted with ether, the ethereal solution washed with water, dried over calcium chloride, distilled to a low bulk, and then poured into excess of benzene. On standing, crystals separated, which were filtered off and dried on a porous tile. From the acid liquid, after extraction with ether, more acid can be obtained through the lead salt, as previously described.

In this way about 3 to 4 grams of a crystalline acid were obtained. This *acid* melted indefinitely at about 117°, but after washing with hot benzene, fused at 145°. It was recrystallised from ether and from water until the melting point was constant, and was then obtained in hard prisms melting sharply at 157° (corr.). The acid is readily soluble in water or alcohol, and moderately so in ether, but on evaporating the ethereal solution an oil is obtained which gradually solidifies; it is insoluble in benzene or light petroleum. A 6 per cent. aqueous solution was optically inactive. On analysis:

0·1338 gave 0·23 CO_2 and 0·073 H_2O. C = 46·9 ; H = 6·1.
0·0922 „ 0·159 CO_2 „ 0·05 H_2O. C = 47·0 ; H = 6·0.
$C_8H_{12}O_6$ requires C = 47·1 ; H = 5·9 per cent.

The analytical results, melting point, and behaviour towards solvents agree with those recorded for *α-ethyltricarballylic acid*, and a mixture of equal parts of the synthetical acid and that obtained by fusion melted at 157° (corr.).

Further evidence as to its identity with α-ethyltricarballylic acid was afforded by an examination of the following derivatives, which agreed in all respects with those recorded in the following paper (p. 1346) for this acid.

The *anhydro-acid*, prepared by heating the acid with excess of acetyl chloride in a reflux apparatus for 2 hours, could only be obtained as an oil soluble in benzene and yielding with aniline an amorphous compound.

The *silver* salt was prepared by adding silver nitrate to an aqueous solution of the ammonium salt. The flocculent precipitate, insoluble in water, was well washed and dried, first on a porous tile, and then at 100°. On analysis :

0·1248 gave 0·0816 CO_2, 0·0246 H_2O, and 0·0768 Ag. C = 17·8 ; H = 2·2 ; Ag = 61·6.
0·1354 gave 0·0836 Ag. Ag = 61·7.
$C_8H_9O_6Ag_3$ requires C = 18·3 ; H = 1·7 ; Ag = 61·7 per cent.

The *calcium* salt was prepared by digesting the aqueous solution of the acid with an excess of calcium carbonate and filtering. The filtrate, when heated to 100°, became a firm jelly which liquefied on cooling. This behaviour has been shown to be very characteristic of calcium α-ethyltricarballylate. The solution of the calcium salt was evaporated to a low bulk in a vacuum and precipitated with alcohol. The precipitate was dried, first on a porous tile and then between blotting paper. On analysis, the air-dried salt furnished the following results :

0·1284 at 150° lost 0·0306 H_2O, and on ignition gave 0·031 CaO.
H_2O = 23·8 ; Ca = 17·3.
$(C_8H_9O_6)_2Ca_3,9H_2O$ requires H_2O = 23·7 ; Ca = 17·5 per cent.

The *copper* salt, prepared in the usual way with copper acetate, was a bluish-green precipitate insoluble in hot water. After drying on a porous tile and then at 120°, it furnished the following results on analysis :

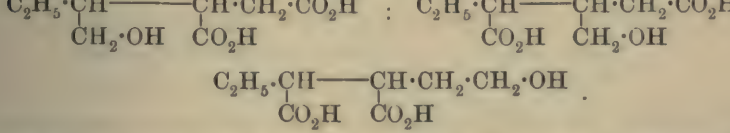
0·0636 gave 0·0256 CuO. Cu = 32·1.
$(C_8H_9O_6)_2Cu_3$ requires Cu = 32·2 per cent.

Constitutional Formulæ of Pilopic and Homopilopic Acids.

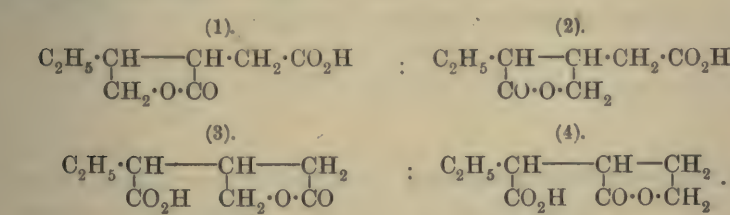
The identification of α-ethyltricarballylic acid as a product of the fusion of homopilopic acid with potassium hydroxide, and the other facts recorded in this paper, render it possible to state with a high degree of probability the constitutional formulæ of both pilopic and homopilopic acids. The formation of acetic and propionic acids by the oxidation of *iso*pilocarpine and of normal butyric acid by the fusion of pilopic acid with potassium hydroxide, prove that the *iso*butyl group does not exist in *iso*pilocarpine, and that the formation of *iso*butyric acid by the fusion of the alkaloid with potassium hydroxide is probably due to the action of the fused alkali on the normal acid first formed. That *iso*pilocarpine must contain the *n*-butyl grouping follows from the formation of α-ethyltricarballylic acid,

$$C_2H_5\cdot CH(CO_2H)\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H.$$

The formation of the tricarboxylic acid from the hydroxydicarboxylic acid (as potassium salt) can only be explained on the assumption that the $CH_2\cdot OH$ group is oxidised to CO_2H. The ethyltricarballylic acid may therefore be derived from one of the three following hydroxydibasic acids:



On account of the stability of homopilopic acid, it is most reasonable to assume that it is a γ-lactonic acid. From the above formulæ, four γ-lactonic acids may be derived:

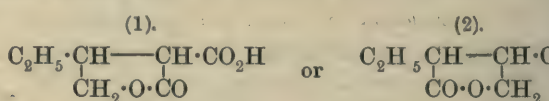


If we regard pilopic acid as derived from homopilopic acid by the loss of carbon dioxide and oxidation of the contiguous carbon atom, only formulæ (1) and (2) are possible, as (3) and (4) would yield acids containing less than seven carbon atoms.

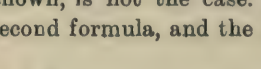
The formation of pilopic acid during the oxidation of *iso*pilocarpine may be assumed to be due either to oxidation of the homopilopic acid first formed, or, as has been previously pointed out, to simultaneous

oxidation at two different points in the molecule. Since, however, both acids contain the *n*-butyl group, it is most probable that they bear the relation to each other previously suggested, since oxidation must have occurred at that portion of the molecule containing the nitrogen atoms. If this argument be admitted, the possible formulæ for pilopic acid will be,

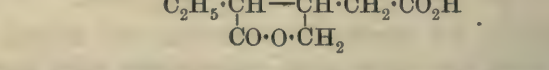
(1). (2).



but of these (1) is clearly not admissible as it is a malonic acid derivative and should therefore lose carbon dioxide on heating at 200°, which, as has been shown, is not the case. There remains therefore for pilopic acid the second formula, and the corresponding formula for homopilopic acid is



Lactonic acids corresponding to these formulæ have not hitherto been prepared, but pilopic acid resembles ethylparaconic acid in many of its physical properties, and the relation between the two is shown by their formulæ:



Pilopic acid. Ethylparaconic acid.

It remains, therefore, to synthesise acids having the constitution assigned to pilopic and homopilopic acids, and to contrast the properties of the acids prepared synthetically with those recorded in this paper. Experiments with this end in view are now in progress.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES.

CXLII.—*A New Synthesis of α-Ethyltricarballylic Acid.*

By HOOPER ALBERT DICKINSON JOWETT.

IN the preceding paper, it was shown that by the fusion of homopilopic acid with potassium hydroxide an acid of the formula $C_8H_{12}O_6$ was formed and that the properties of this acid corresponded with those of α-ethyltricarballylic acid. As, however, two different melting points have been assigned to this acid and as no derivatives have been described other than the silver salt, it was necessary to prepare the

substance and to examine it more fully, so as to be able to identify completely the acid formed from homopilopic acid with the synthetical compound.

α-Ethyltricarballylic acid was first prepared by Auwers (*Ber.*, 1891, **24**, 307, 2897) by the condensation of ethyl ethylsodiomalonate with ethyl fumarate and subsequent hydrolysis. The acid, after recrystallisation, melted at 147—148° and was readily soluble in water, but only moderately so in ether; on evaporation, the ethereal solution left an oil which became crystalline. The substance was prepared more recently by Michael (*Ber.*, 1900, **33**, 3745) by the same method, but he found that after further purification it melted at 155—157°.

In order to prepare the acid for the purpose of comparison, it was deemed advisable to accomplish the synthesis by an entirely different method, as this at the same time would afford additional proof of the correctness of the constitution of the synthetical acid prepared by Auwers.

Ethyl α-cyano-β-ethylsuccinate was prepared by the general method of preparation of the alkyl-substituted succinic acids described by Bone and Sprankling (Trans., 1899, **75**, 839), by condensing the sodium compound of ethyl cyanoacetate with ethyl α-bromobutyrate.

The sodium compound of ethyl α-cyano-β-ethylsuccinate was then condensed with ethyl bromoacetate with the formation of ethyl β-cyano-α-ethyltricarballylate. This stage of the synthesis may be presented by the following equation:

$$CH_2Br\cdot CO_2Et + CO_2Et\cdot CNa(CN)\cdot CH(C_2H_5)\cdot CO_2Et = CO_2Et\cdot CH_2\cdot C(CN)(CO_2Et)\cdot CH(C_2H_5)\cdot CO_2Et + NaBr.$$

The ethyl cyanoethyltricarballylate, on hydrolysis, yielded an acid from which carbon dioxide was eliminated by heating at 180° with the formation of α-ethylcarballylic acid.

These condensations took place readily, the yield of cyano-esters in the first and second stages of the synthesis being 50 and 70 per cent. respectively of the calculated amounts. As these cyano-esters have not been previously prepared, their boiling points and densities were determined.

α-Ethyltricarballylic acid as thus prepared was found to agree in its general properties with those previously recorded, and after recrystallisation melted at 157° (corr.), thus confirming the figure given by Michael. Of its derivatives described later, the calcium salt is very characteristic; it is fairly soluble in cold water, but on warming the aqueous solution, the liquid is converted into a solid jelly, which liquefies on cooling. This gelatinisation of the calcium salt, coupled with the melting point of the acid, affords the best means of identifying the substance.

Experimental.

Ethyl α-Cyano-β-ethylsuccinate, $CO_2Et{\cdot}CH(CN){\cdot}CH(C_2H_5){\cdot}CO_2Et$.

This ester was prepared as follows:—28·5 grams of ethyl cyanoacetate were mixed with a solution of 5·75 grams of sodium in 70 grams of absolute alcohol, and to the resulting thick paste 48·75 grams of ethyl α-bromobutyrate were added. The mixture, which became warm, was heated on a water-bath until neutral, which generally required 2—3 hours; it was then cooled, poured into water, and the oil which separated was extracted with ether. The ethereal solution was washed with water, dried over calcium chloride, and then distilled. The residual oil was fractionated under 20 mm. pressure, when a quantity of unchanged ethyl cyanoacetate and ethyl α-bromobutyrate distilled below 100°, but the greater portion of the liquid distilled at 160—170°, leaving only a very small residue in the flask. On refractionation, the portion distilling at 160—170° was collected. Of this a portion boiling constantly at 167—168° was set aside for analysis; it had a density d 15°/15° = 1·0647. The yield of product boiling at 160—170° under 20 mm. pressure was 50 per cent. of the theoretical. On analysis:

0·1338 gave 0·285 CO_2 and 0·0916 H_2O. C = 58·1; H = 7·6.
0·1512 „ 9·4 c.c. nitrogen at 24° and 764 mm. N = 6·8.
$C_{11}H_{17}O_4N$ requires C = 58·1; H = 7·5; N = 6·2 per cent.

The correctness of the formula ascribed to the cyano-ester was proved by the fact that on hydrolysis the compound furnished ethylsuccinic acid melting at 98°, which on analysis yielded the following result:

0·132 gave 0·2372 CO_2 and 0·086 H_2O. C = 49·0; H = 7·2.
$C_6H_{10}O_4$ requires C = 49·3; H = 6·9 per cent.

The characteristic calcium ethylsuccinate was also prepared.

Ethyl β-Cyano-α-ethyltricarballylate,
$CO_2Et{\cdot}CH(C_2H_5){\cdot}C(CN)(CO_2Et){\cdot}CH_2{\cdot}CO_2Et$.

This cyano-ester was prepared as follows:—To 6 grams of sodium dissolved in 60 grams of absolute alcohol, 45·4 grams of ethyl-α-cyano-β-ethylsuccinate were added. The mixture became warm and very viscid, but no solid separated; after cooling, 33·4 grams of ethyl bromoacetate were added, when a reaction at once took place with evolution of heat and separation of sodium bromide. The mixture was heated for half-an-hour on a water-bath, cooled, and then poured into water. The oil which separated was extracted with ether, the ethereal solution washed with water, dried with calcium chloride, and distilled. The residual oil was carefully fractionated under 20 mm. pressure. Scarcely

any liquid distilled below 195°, the greater portion came over between 195° and 215°, leaving a small residue in the flask. On refractionation, the portion distilling at 205—208° under 17—21 mm. pressure was collected, the greater portion, boiling constantly at 208° under 21 mm. pressure, being put aside for analysis and for the determination of its density. The yield of refractionated product was 70 per cent. of the theoretical. On analysis :

0·1716 gave 0·3602 CO_2 and 0·1144 H_2O. C = 57·3 ; H = 7·4.
0·1756 „ 7·5 c.c. nitrogen at 24° and 764 mm. N = 4·7.
$C_{15}H_{23}O_6N$ requires C = 57·5 ; H = 7·3 ; N = 4·5 per cent.

The density at 16° compared with water at 16° was 1·0972.

α-Ethyltricarballylic Acid, $CO_2H{\cdot}CH(C_2H_5){\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$.

This acid was obtained from the ethyl cyanoethyltricarballylate in the following manner. The ester was first boiled with five times its weight of 40 per cent. aqueous sulphuric acid in a reflux apparatus until all the oily drops had disappeared, which generally required a period of 24—48 hours. The acid liquid was then saturated with ammonium sulphate and extracted with ether six times. The ethereal extract was distilled to a convenient bulk and extracted with dilute sodium carbonate solution. This was acidified with sulphuric acid, saturated with ammonium sulphate, and extracted with ether. The ethereal solution was washed with water, dried with calcium chloride, distilled to a low bulk, and then poured into ten times its volume of benzene. On standing, crystals separated which were filtered off ; these, when dried, melted at 117° with effervescence. The acid was then heated in a small flask in a paraffin bath at 180° until all evolution of gas had ceased. After cooling, the mass was dissolved in a little hot water, boiled with animal charcoal, and filtered. On standing and stirring with a glass rod, the solution became pasty. The crystals were drained on a porous tile and recrystallised from a little water until of constant melting point ; thus purified, they melted at 156—157° (corr.). The pure acid required about 20 times its weight of ether to dissolve it, but on evaporating this solution at the ordinary temperature, no crystals separated until all the ether had evaporated, when an oil was left which gradually became solid. On analysis :

0·1974 gave 0·341 CO_2 and 0·106 H_2O. C = 47·1 ; H = 6·0.
0·198 „ 0·342 CO_2 „ 0·1064 H_2O. C = 47·1 ; H = 6·0.
$C_8H_{12}O_6$ requires C = 47·1 ; H = 5·9 per cent.

The *anhydro-acid* was prepared by adding the acid to three times its weight of acetyl chloride and boiling for 2 hours in a reflux apparatus. The acid slowly dissolved and the excess of acetyl chloride was removed

by evaporation on the water-bath and subsequent standing in a vacuous desiccator over solid potassium hydroxide. In this way, a hard, sticky varnish was obtained, which could not be crystallised. On analysis :

0·2218 gave 0·4146 CO_2 and 0·1108 H_2O. C = 51·0 ; H = 5·5.
$C_8H_{10}O_5$ requires C = 51·6 ; H = 5·4 per cent.

The anhydro-acid dissolved in benzene ; on the addition of aniline to the solution, heat was developed, the liquid immediately became cloudy, and an amorphous precipitate separated which, however, could not be obtained crystalline.

The *barium* salt was prepared by digesting an aqueous solution of the acid with excess of barium carbonate until neutral, and filtering. On warming the filtrate, crystals appeared which, however, redissolved on cooling. The filtrate was evaporated to a small bulk, filtered while hot, and the crystals dried, first on a porous tile and finally between blotting paper. Analysis showed that the air-dried crystals contained 7 mols. of water of crystallisation, of which six are removed by heating at 180° :

0·3156 at 180° lost 0·036 H_2O and gave 0·234 $BaSO_4$. H_2O = 11·4 ; Ba = 43·6.
0·1716 gave on combustion 0·0526 H_2O. H = 3·4.
$(C_8H_9O_6)_2Ba_3,7H_2O$ requires H_2O = 13·4 ; Ba = 43·8 ; H = 3·4 per cent.

The *calcium* salt was prepared by digesting an aqueous solution of the acid with excess of calcium carbonate and filtering. The filtrate had the remarkable property of becoming a firm jelly when heated to 100°, and liquefying on cooling. The liquid was evaporated to a small bulk in a vacuum and the calcium salt precipitated with alcohol in a microcrystalline form. On analysis :

0·1886 at 150° lost 0·044 H_2O and on ignition gave 0·0454 CaO. H_2O = 23·3 ; Ca = 17·2.
$(C_8H_9O_6)_2Ca_3,9H_2O$ requires H_2O = 23·7 ; Ca = 17·5 per cent.

The *copper* salt, prepared by adding copper acetate solution to an aqueous solution of the ammonium salt of the acid and boiling, was a greenish-blue, flocculent precipitate. On analysis ;

0·1972 at 150° lost 0·0272 H_2O and on ignition gave 0·0696 CuO. H_2O = 13·8 ; Cu = 28·2.
$(C_8H_9O_6)_2Cu_3,5H_2O$ requires H_2O = 13·2 ; Cu = 28·0 per cent.

The *triethyl ester*, prepared in the usual manner by the action of sulphuric acid and ethyl alcohol on the acid, was a limpid, colourless liquid boiling at 170—175° under 16 mm. pressure. On analysis, it furnished the following results :

0·2136 gave 0·457 CO_2 and 0·1574 H_2O. C = 58·3; H = 8·2.
$C_{14}H_{24}O_6$ requires C = 58·3; H = 8·3 per cent.

An attempt to prepare the amide by mixing the ester with excess of strong ammonia was unsuccessful.

Addendum.—Since this paper was in type the author has received a communication from Dr. Bone pointing out the following passage in a paper, "Researches on the Alkyl Substituted Succinic Acids," by Bone and Sprankling (Trans., 1899, 75, 864): "Finally, we are studying the interaction of the sodium derivative of ethylic cyanosuccinates and the ethylic salts of α-bromo-fatty acids."

As the purpose for which reference was made to the paper in question only necessitated the reading of that portion of it relating to the details of preparation of the analogous ethyl cyanomethylsuccinate, the concluding paragraph containing the passage referred to most unfortunately escaped my attention.

The necessity for the preparation of α-ethyltricarballylic acid and certain of its derivatives was due to the great importance of identifying beyond question the acid formed by the fusion of homopilopic acid with potassium hydroxide.

The Wellcome Chemical Research Laboratories.

CXLIII.—*Benzoylation of Fatty Acids in the Presence of Ammonia. Formation of Amides.*

By K. J. P. Orton.

It was recently shown (Orton and Garrod, *J. Physiol.*, 1901, 27, 89) that *p*-dibenzoxyphenylacetamide was formed in the benzoylation, by the Schotten-Baumann method, of an abnormal urine, the so-called "alcapton-urine," which contains *p*-dihydroxyphenylacetic acid (homogentisic acid), and it was further demonstrated that the production of this amide depended on the presence of ammonia in the urine.

Investigation has proved that many acids under similar conditions yield an amide. Thus, from stearic, phenylacetic, *p*-nitrophenylacetic, and cinnamic acids, amides are formed, whilst *p*-aminophenylacetic, *p*-hydroxyphenylacetic, and mandelic acids are both benzoylated and converted into amides. Tyrosine yields dibenzoyltyrosinamide. Aromatic acids, for example, benzoic and toluic acids, do not yield amides. If, instead of ammonia, an aqueous solution of methylamine is used, the corresponding methylamides are obtained.

The benzoylation was carried out in the following way. To a dilute ammoniacal solution of the acid (1 part) is added excess of benzoyl chloride (2—3 parts); a 10 per cent. solution of sodium hydroxide is introduced in successive portions, and the mixture well shaken until the smell of benzoyl chloride is no longer perceptible. As the benzoyl chloride disappears, a solid separates, which is a mixture of benzamide and the amide of the acid. The quantity of the former is but small, when only sufficient ammonia to dissolve the acid has been used; excess of ammonia increases the proportion of benzamide.

The yield of amide (or methylamide) is generally small and does not exceed 25 per cent. of the calculated amount except in one or two cases.

If the acid and benzoyl chloride are heated together for 2 or 3 hours at 100—120° and the mixture then treated with a solution of sodium hydroxide and ammonia (or methylamine), the yield is much increased, and frequently amounts to 75 per cent. of the acid used.

One or two explanations of the above reaction suggest themselves. It may be supposed that an anhydride is first formed, either a compound anhydride of benzoic acid and the fatty acid, or a simple anhydride of the fatty acid; thus:

$$C_6H_5\cdot COCl + R\cdot CO\cdot OH = C_6H_5\cdot CO\cdot O\cdot CO\cdot R + HCl \text{ or}$$
$$2R\cdot CO\cdot OH + C_6H_5\cdot COCl = (R\cdot CO)_2O + C_6H_5\cdot CO\cdot OH + HCl.$$

On the other hand, the benzoyl chloride may interact with the acid, forming benzoic acid and the chloride of the acid, thus:

$$C_6H_5\cdot COCl + R\cdot CO\cdot OH = C_6H_5\cdot CO\cdot OH + R\cdot COCl.$$

Bauer (*Inaug. Dissert. Tübingen*, 1901) records the fact that benzoic anhydride is formed when benzoyl chloride is shaken with a solution of sodium hydrogen carbonate. In a patent of Knoll & Co. (D.R.-P. 117267), the production of compound anhydrides from acid chlorides and acids in the presence of alkali carbonates is mentioned. Further, according to Béhal (*Compt. rend.*, 1899, **129**, 681), acetic benzoic anhydride yields acetamide and benzoic acid with ammonia. From these facts, it seems probable that a compound anhydride of benzoic and the fatty acid (or possibly a simple anhydride of the fatty acid) is formed when the acid is treated with benzoyl chloride in presence of sodium hydroxide, and that this anhydride reacts with ammonia, producing benzoic acid and the amide of the fatty acid.

When the fatty acid is heated with benzoyl chloride, the chloride of the fatty acid may be formed, and in support of this view, Polzenius (*Chem. Zeit.*, 1896, **20**, 46) has observed that benzoyl chloride and acetic acid at 110° yield benzoic acid and acetyl chloride. With phenylacetic and mandelic acids, at least, this does not appear to

be the case. Molecular proportions of phenylacetic acid and benzoyl chloride (19 grams of each) were heated together for about 2 hours at 120° and for a short time at 150°. As soon as the hydrogen chloride, which was at first rapidly evolved, ceased to be given off, the mixture was distilled under 28 mm. pressure in order to isolate phenylacetyl chloride (b. p. 102·5° under 17 mm.); 2·5 grams of an oil passed over at 110—140°, and appeared to be chiefly benzoyl chloride and to contain little, if any, phenylacetyl chloride.* The residue in the flask, which was nearly free from acid chloride, did not solidify on cooling and could not be crystallised from any solvent. After 2 or 3 days, crystals of benzoic acid began to separate. When the oil is boiled with water, benzoic and phenylacetic acids are formed. With ammonia, the oil reacted with development of heat and immediately solidified. The solid was nearly pure phenylacetamide (m. p. 152°), and on acidifying the ammoniacal mother liquor, benzoic acid separated. Aniline similarly yielded phenylacetanilide (m. p. 117°) and benzoic acid; no trace of benzanilide was discovered.

From this experiment, it would seem probable that an unstable compound anhydride is also the main product when the acid chloride and acid are heated together.

Further experiments on the preparation and reactions of these compound anhydrides are in progress.

p-*Nitrophenylacetmethylamide*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NH \cdot CH_3$.—*p*-Nitrophenylacetic acid (1 gram) was heated with benzoyl chloride (2 grams) on the water-bath for 2 hours. A little water was poured on the oil, and 3 c.c. of a 33 per cent. aqueous solution of methylamine added. The mixture was then shaken with a 10 per cent. aqueous solution of sodium hydroxide, introduced in successive portions, until the odour of benzoyl chloride had disappeared. The solid remaining was collected, washed with water, and recrystallised from boiling water. The methylamide crystallises in long, silky, colourless needles melting at 159°, and is very soluble in all solvents, except water and petroleum. It is slowly hydrolysed by boiling aqueous sodium hydroxide, but rapidly by an alcoholic solution, with evolution of methylamine.

0·1472 gave 19 c.c. moist nitrogen at 23° and 765 mm. N = 14·51.
$C_9H_{10}O_3N_2$ requires N = 14·43 per cent.

p-*Benzoylaminophenylacetamide*, $C_6H_5 \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NH_2$. —This amide is readily formed when *p*-aminophenylacetic acid is benzoylated by the Schotten-Baumann method in the presence of ammonia. Two grams of the acid were dissolved in 20 c.c. of 10 per

* The boiling points of these acid chlorides lie very near together.

cent. ammonia; to the solution was added excess of benzoyl chloride (5 c.c.), and the mixture then shaken with sodium hydroxide. The solid was collected, washed with water, and recrystallised from alcohol. The amide crystallises in small plates melting at 248°, and only slightly soluble in all solvents. One gram of the pure amide was obtained; the yield is not increased when the acid and benzoyl chloride are heated before treatment with ammonia and sodium hydroxide.

0·1048 gave 0·2716 CO_2 and 0·0533 H_2O. C = 70·68; H = 5·65.
0·1103 ,, 10·8 c.c. moist nitrogen at 20° and 771 mm. N = 11·30.
$C_{15}H_{14}O_2N_2$ requires C = 70·86; H = 5·51; N = 11·02 per cent.

On hydrolysing the amide with alkalis or acids, *p*-aminophenylacetic and benzoic acids were always formed.

p-*Benzoylaminophenylacetic Acid*, $C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot CH_2\cdot CO_2H$, is formed when *p*-aminophenylacetic acid is benzoylated by the Schotten-Baumann method. The clear alkaline solution, obtained when all the benzoyl chloride has disappeared, was acidified with acetic acid. The solid which separated was dissolved in alcohol, and crystallised therefrom in tufts of needles melting at 205—206°.

0·1424 gave 7·1 c.c. moist nitrogen at 19° and 767 mm. N = 5·78.
$C_{15}H_{13}O_3N$ requires N = 5·48 per cent.

p-*Benzoxyphenylacetamide*, $C_6H_5\cdot CO\cdot O\cdot C_6H_4\cdot CH_2\cdot CO\cdot NH_2$, is best prepared by heating *p*-hydroxyphenylacetic acid and benzoyl chloride before treatment with ammonia and sodium hydroxide. The solid was washed with ether and then recrystallised three or four times from alcohol, in which it is only slightly soluble. It forms microscopic crystals which melt at 167—169°.

0·1808 gave 8·1 c.c. moist nitrogen at 16° and 763 mm. N = 5·34.
$C_{15}H_{13}O_3N$ requires N = 5·48 per cent.

Sufficient material for the preparation of *p*-benzoxyphenylacetic acid was not available.

Benzoylmandelamide (*phenylbenzoylglycollamide*),
$C_6H_5\cdot CH(O\cdot CO\cdot C_6H_5)\cdot CO\cdot NH_2$,
is easily prepared from the calculated amount of mandelic acid and to the extent of about 75 per cent. when the acid and benzoyl chloride are heated together at 120°, before the addition of ammonia and sodium hydroxide. After the benzoyl chloride has disappeared, a sticky semi-solid mass remains, which after washing with ether becomes a white, crystalline solid. On recrystallisation from water or dilute alcohol, the amide is obtained pure in tufts of silky needles melting at 162°, and readily soluble in alcohol, chloroform, or benzene, but only slightly so in petroleum, cold water, or ether.

0·1996 gave 10 c.c. moist nitrogen at 21° and 765 mm. N = 5·71.
$C_{15}H_{13}O_3N$ requires N = 5·48 per cent.

Benzoylmandelmethylamide, $C_6H_5\cdot CH(O\cdot CO\cdot C_6H_5)\cdot CO\cdot NH\cdot CH_3$, is prepared and purified exactly as the amide, methylamine replacing ammonia. It crystallises from dilute alcohol or water in tufts of needles melting at 139°.

0·1970 gave 9·4 c.c. moist nitrogen at 18° and 760 mm. N = 5·48.
$C_{16}H_{15}O_3N$ requires N = 5·2 per cent.

All attempts to obtain benzoylmandelic acid from the amide failed. Aqueous hydrochloric acid attacks it very slowly, whilst the alcoholic acid converts it rapidly into ethyl benzoate and mandelate. Seventy-five per cent. nitric acid containing nitrous acid—the reagent which so satisfactorily converted dibenzoxyphenylacetamide into dibenzoxyphenylacetic acid (*loc. cit.*)—produces only benzoic acid. Alkalis bring about complete hydrolysis. Mandelic acid could not be benzoylated by the Schotten-Baumann method with sodium hydroxide or sodium hydrogen carbonate, or by use of pyridine in the manner recommended by Einhorn and Hollandt (*Annalen*, 1898, 301, 95). On heating mandelic acid with benzoyl chloride at 110°, an oil is obtained which decomposes with water or alkalis, but with ammonia gives benzoylmandelamide.

Cinnamic Methylamide, $C_6H_5\cdot CH{:}CH\cdot CO\cdot NH\cdot CH_3$, is obtained, in the manner previously described, as a pasty mass, which solidifies on cooling with ice. It crystallises from hot water in plates melting at 111°, and is very soluble in all solvents, except water and petroleum.

0·1856 gave 14·9 c.c. moist nitrogen at 25° and 764 mm. N = 8·9.
$C_{10}H_{11}ON$ requires N = 8·7 per cent.

Dibromocinnamic Methylamide, $C_6H_5\cdot CHBr\cdot CHBr\cdot CO\cdot NH\cdot CH_3$.—To a solution of cinnamic methylamide (1 mol.) in chloroform, a solution of bromine (1 mol.) in the same solvent was slowly added. The colour of the bromine rapidly disappeared and crystals separated; these were dissolved in alcohol, from which they crystallised in lustrous, colourless prisms. On heating, the dibromo-compound becomes coloured at 200°, and melts and decomposes at 214°.

0·1456 gave 0·1700 AgBr. Br = 49·67.
$C_{10}H_{11}ONBr_2$ requires Br = 49·84 per cent.

Dibenzoyltyrosinamide,
$C_6H_5\cdot CO\cdot O\cdot C_6H_4\cdot CH_2\cdot CH(NH\cdot CO\cdot C_6H_5)\cdot CO\cdot NH_2$.
—One gram of tyrosine was dissolved in 10 c.c. of a 10 per cent. solution of ammonia and 2 c.c. of benzoyl chloride were added. After

shaking with caustic soda until the benzoyl chloride had disappeared, the solid was filtered and washed with water and then with ether. The amide crystallises from dilute alcohol in nests of small, lustrous needles melting at 246°, and is moderately soluble in alcohol or chloroform. It is decomposed only slowly with evolution of ammonia by boiling concentrated alkali hydroxides; in the presence of alcohol, the action is more rapid and tyrosine and benzoic acid are formed besides ammonia.

0·107 gave 0·278 CO_2 and 0·0445 H_2O. C = 70·86 ; H = 4·62.
0·0962 „ 6·0 c.c. moist nitrogen at 20·5° and 754 mm. N = 7·3.
$C_{23}H_{20}O_4N_2$ requires C = 71·1 ; H = 5·1 ; N = 7·2 per cent.

Stearamide, $C_{17}H_{35}{\cdot}CO{\cdot}NH_2$, was first prepared by Carlet (*Jahresber.*, 1859, 367) from ethyl stearate and ammonia. It can be very easily obtained by heating stearic acid and benzoyl chloride at 110—120° and subsequently treating the mixture with ammonia and sodium hydroxide. From chloroform, it crystallises in nests of needles melting at 106—107°.

This reaction has been tried with many other acids. Dicarboxylic aliphatic acids appear not to yield an amide, or at least only in very small quantities. From sulphonic acids, derivatives are obtained, but so far only in small amount.

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CXLIV.—*Liquid Nitrogen Peroxide as a Solvent.*

By Percy Faraday Frankland, Ph.D., F.R.S., and Robert Crosbie Farmer, M.Sc. (Vict.), Ph.D.

The object of the following investigation was to ascertain more accurately than has hitherto been attempted the properties of liquefied nitrogen peroxide as a solvent; in particular to determine to what extent organic compounds can be dissolved in it without decomposition and in the cases where they are attacked to ascertain the nature of the reaction.

The question presented itself, whether substances dissolved in liquefied nitrogen peroxide exist in the normal state of molecular aggregation or whether they undergo electrolytic dissociation on the one hand, or associate themselves to complex molecules on the other.

Nitrogen peroxide is a comparatively easily liquefiable gas. As it boils at 21°, it can be readily condensed in an ordinary freezing

mixture. It can therefore be easily purified by redistillation and can be boiled for many hours in an ebullioscopic apparatus without any serious loss, if the vapour be condensed by means of a freezing mixture.

Its reactions and properties can be examined with ease at a temperature a little below 0°, and the pure solvent may be recovered from its solutions by distillation.

The chief difficulty met with in working with this solvent was the extreme rapidity with which it attacks india-rubber and cork. This rendered it necessary to use glass connections in almost all cases, since rubber and cork were destroyed in a very short time, even when protected as well as possible by a coat of vaseline or paraffin wax. In some cases, connections could be made with asbestos paper coated with vaseline.

A review of the literature on the subject of liquid nitrogen peroxide reveals very little work on the solvent powers of this substance. The chemical activity of nitric acid, when brought in contact with organic compounds, seems to have led to the belief that nitrogen peroxide would be still more active, and that very few organic compounds would be able to withstand its action. Thus Ramsay (Trans., 1890, 57, 592), in his work on the depression of the freezing point of nitrogen peroxide by dissolved substances, mentions chloroform and chlorobenzene as being "among the few available and unobjectionable substances which are not acted on by nitrogen peroxide."

We have, therefore, been somewhat surprised to find that liquid nitrogen peroxide is not only a remarkably good solvent for most organic compounds, but also a comparatively inert substance in the pure anhydrous condition.

It is probable that many previous workers have made their observations with slightly impure nitrogen peroxide, and this would account for their statements to the effect that it attacks most organic compounds, for it has also been our experience that although the pure nitrogen peroxide is comparatively inert, yet the slightly impure product, that is, a product which has not been completely dehydrated or which contains traces of lower oxides, is much more active and frequently attacks compounds which are unaffected by the pure peroxide; thus cane sugar was soluble without decomposition in the pure solvent but was very quickly attacked when the nitrogen peroxide contained traces of water.

In its general behaviour, liquid nitrogen peroxide shows a considerable resemblance to the common organic solvents. Inorganic salts were found to be quite insoluble in it, whereas most organic compounds dissolved with at least the same ease as in ether. As will be seen later, many of these were unacted on, although in some cases nitration, oxidation, &c., set in.

It was thus possible, in the case of many organic compounds, to examine the solutions as regards electric conductivity, and further to determine the molecular weights of a number of compounds by the rise of boiling point.

The electric conductivity of the solutions was measured in order to ascertain whether ionic dissociation occurs to any appreciable extent when substances are dissolved in nitrogen peroxide. Recent researches have shown that a number of hitherto unsuspected liquids act as "ionising solvents." In particular, the interesting researches of Walden on liquefied sulphur dioxide (*Ber.*, 1899, **32**, 2862), and of Franklin and Kraus on liquefied ammonia (*Amer. Chem. J.*, 1899, **23**, 277; 1900, **24**, 83) have shown that these liquids dissociate dissolved substances to a considerable extent. Many other cases of ionising solvents have also come to light in recent years (compare *Amer. Chem. J.*, 1901, **25**, 232).

The probability that liquefied nitrogen peroxide would also prove to be an ionising solvent formed the original inducement to the following investigation, and the fact that Bouty (*Compt. rend.*, 1888, **106**, 595) found solutions in pure nitric acid to be good conductors of electricity seemed to justify this expectation. When it was found, however, that liquid nitrogen peroxide did not dissolve inorganic salts, whereas it readily dissolved indifferent organic compounds, it seemed more probable that it resembled such organic solvents as benzene in its behaviour. This has been borne out by experiment.

The electric conductivity of nitrogen peroxide itself has already been measured by Boguski (*Zeit. physikal. Chem.* 1890, **5**, 69), who found that the pure peroxide is a non-conductor, but that when a little water is added the electric conductivity increases enormously. No experiments appear to have been made with solutions in liquid nitrogen peroxide. We find the solutions in the liquid nitrogen peroxide to be to all intents and purposes absolute non-conductors. The dissolved substances do not, therefore, exist to any appreciable extent in the ionised state. On the contrary, as will be shown, many compounds are associated to complex molecules when dissolved in this liquid.

The experiments were all carried out with acids, bases being attacked immediately and salts being insoluble. In every case, it was found that the solutions conducted just as little as the pure solvent. It may therefore be safely concluded that liquid nitrogen peroxide is not an ionising solvent.

In order to examine the state of molecular aggregation of substances dissolved in this liquid more fully, we have made a number of molecular weight determinations by observing the influence on the boiling point of the substances dissolved. The constant was first ascertained by means of a series of experiments in which solutions of indifferent

organic compounds were employed. Various acids were then examined and in many cases these were found to be associated to double molecules. Nitrogen peroxide therefore resembles benzene and some other organic liquids in its power of associating many dissolved hydroxy-compounds. This is, we believe, the first case in which an inorganic solvent has been found to bring about an association of dissolved substances.

Experimental.

For the preparation of liquid nitrogen peroxide, the method described by Cundall (Trans., 1891, 59, 1077) was found to be the most satisfactory. The method of heating dry lead nitrate was at first employed, as it gives a very pure product. The yield is, however, only moderately satisfactory, and moreover, the tube in which the lead nitrate is heated occasionally becomes stopped up and necessitates breaking off the experiment.

The method described by Cundall, in which arsenic trioxide is heated with a mixture of sulphuric acid and fuming nitric acid, gives a product containing lower oxides of nitrogen; these can, however, be completely oxidised to the peroxide by prolonged treatment with a current of oxygen.

Some care must be taken during the early part of the reaction, as it is liable to become too violent. The arsenic trioxide should be used in lumps of moderate and uniform size and should not contain any fine powder. The heating must be conducted very slowly and carefully and it is advisable to have a basin of ice-water at hand, as it is occasionally necessary to cool down the flask in order to check the violence of the reaction.

The reaction proceeds in two stages, which are fairly sharply defined. In the first of these, practically all the nitrous fumes are absorbed by the sulphuric acid and very little nitrogen peroxide, if any, collects in the receiver. This stage of the reaction proceeds at a fairly low temperature and requires considerable attention, as it easily becomes too violent. In the second stage, a higher temperature is employed, in order to break up the nitrososulphuric acid with the formation of nitrogen peroxide. This heating may be commenced as soon as the mixture in the flask ceases to evince a tendency to react too violently when warmed. The reaction is endothermic and no more danger is to be feared of the reaction becoming uncontrollable. A copious stream of nitrogen peroxide is evolved. This is first passed through a short reflux condenser cooled by water and then through a glass worm cooled to about $-10°$, and condenses with practically no loss, even though the distillation be carried on very quickly. After a time, the evolution of nitrogen

peroxide nearly ceases and it is best to break off the experiment at this point. If the heating be continued, a third stage sets in and nitric oxide is evolved. If this be passed into the receiver, it reduces part of the nitrogen peroxide already collected, forming a green solution.

The distillate is dehydrated by the addition of phosphoric oxide and further purified by the prolonged action of a current of dry oxygen at a low temperature. The purified liquid, which must be perfectly free from all tinge of green, is then redistilled and kept in stoppered bottles containing phosphoric oxide.

I. Nitrogen Peroxide as a Solvent.

In order to examine the solvent powers of liquefied nitrogen peroxide on various substances, a few grams of the peroxide were brought into a carefully-dried tube and cooled in a freezing mixture. The substance to be examined was then gradually introduced in a fine, dry powder and its behaviour noted. If it dissolved, so much was added that a nearly saturated solution was formed and the clear liquid was then evaporated down, the nitrogen peroxide being recovered by means of a spiral condenser in a freezing mixture. The last traces of the peroxide were removed as completely as possible by exhausting the tube, and warming it at the same time. The residue was then examined as regards melting point and other properties, in order to ascertain whether any reaction had occurred.

Various other methods were employed in order to detect traces of reaction which might be overlooked in examining the residue obtained by evaporation. In general, any decomposition which an organic compound undergoes shows itself by a green colour which the nitrogen peroxide assumes. In the case of simple oxidations, this is due to the formation of the trioxide by the reduction of the peroxide. In cases where a hydrogen atom is displaced, the water formed also acts on the nitrogen peroxide to form a bright green liquid. The formation of this green tinge is therefore a sensitive indication that a reaction has taken place.

In the cases in which water is set free, a more delicate indication is given by the electric conductivity. As already mentioned, the smallest trace of water causes the conductivity to rise enormously.

A third, and also very sensitive, method was to ascertain whether the boiling point of the liquid rose in accordance with Raoult's law. If no decomposition occurred, the normal rise of boiling point was observed. If, however, any decomposition took place, the boiling point fell instead of rising owing to the formation of lower oxides in the solution.

It is well known that most of the metals are quickly attacked by nitrogen peroxide. Of the non-metals, *chlorine* is soluble to some extent, *bromine* is miscible in all proportions, forming a brown solution, whilst *iodine* dissolves with extreme ease, forming a purple-brown solution. *Sulphur*, on the other hand, is only slightly soluble. No reaction takes place between these elements and nitrogen peroxide.

Inorganic Compounds.

(i) *Salts.*—No case was found in which an inorganic salt was soluble in nitrogen peroxide. In most of the cases examined, the salts were found to be unacted on by treatment with this reagent. Here again, however, the inertness depends on the complete purity of the peroxide. It was found, for instance, that chlorides were attacked moderately quickly by nitrogen peroxide which had not been completely dehydrated, with evolution of chlorine, but that when pure peroxide was used, no action took place. The general behaviour of liquid nitrogen peroxide towards inorganic salts will be seen by the following results.

Potassium nitrate, *sulphate*, and *chlorate*, *sodium nitrite*, *mercuric nitrate*, and *hydrazine sulphate* were neither dissolved nor attacked by the liquid peroxide. Of the halogen compounds, the *fluorides* and *chlorides* were unaffected by the pure anhydrous liquid. Potassium chloride was quickly attacked in presence of traces of moisture, with evolution of chlorine, which partly escaped and partly remained dissolved in the liquid peroxide. *Potassium bromide* and *iodide* were both attacked, even by the pure anhydrous liquid; the halogen set free remained in solution. *Ferric chloride* was examined, as it is well known to be somewhat soluble in ether. When dried with great care, the ferric chloride remained unaffected by the liquid, but in presence of traces of moisture it was quickly attacked and the solution was found afterwards to contain traces of iron.

The iron compounds of the diketones were also examined on account of the interest which they possess as being pseudo-salts, non-ionised in aqueous solution and dissolving easily in indifferent organic solvents. The deep-red iron compounds of *acetonylacetone*, $Fe(C_6H_9O_2)_3$, and *benzoylacetone*, $Fe(C_{10}H_9O_2)_3$, were employed, but were both immediately attacked and no iron was found in the solution.

Mercuric cyanide was tried as being a further example of a pseudo-salt, but remained entirely unaffected.

It may be stated in general that inorganic salts are undissolved and in the majority of cases unattacked by liquid nitrogen peroxide.

(ii) *Inorganic Acids.*—Aqueous hydrochloric acid has been long known to react with nitrogen peroxide, forming nitric acid and aqua

regia. The behaviour of dry *hydrogen chloride* does not appear to have been examined. We find it to be entirely without action, as was shown by the fact that the solution showed no green tinge and possessed no measurable electric conductivity.

Sulphuric acid remained at first unaffected. Gradually, however, it combined with the peroxide to form a solid mass of 'chamber crystals' with evolution of heat.

Phosphoric acid was found to absorb some nitrogen peroxide. The resulting compound was insoluble in nitrogen peroxide, but could not be induced to crystallise, and its composition is therefore at present unknown. It appears, however, to be a nitrosophosphoric acid, as it reacts with water in exactly the same way as nitrososulphuric acid, with evolution of nitrous fumes.

Boric and *iodic acids* were unattacked and undissolved by nitrogen peroxide.

Organic Compounds.

As inorganic salts were found to be insoluble in liquid nitrogen peroxide, its effect on organic compounds was next examined. It was at first thought that almost all organic compounds would be immediately acted on when brought together with the liquid, and considerable precautions were taken when introducing the substances.

The liquid was, however, soon found to be surprisingly inert. A great many organic substances can be introduced into it with impunity and it is only in exceptional cases that it reacts with such violence as to render the experiments in any way difficult to carry out. As was to be expected, the presence of small quantities of water increased the chemical activity of the peroxide greatly. Many of the following substances which were unattacked by the pure peroxide were decomposed by treatment with a product containing traces of water.

As a solvent, nitrogen peroxide takes up most organic compounds with considerable ease. In some cases, the compounds were so easily soluble that they only crystallised out when almost all the nitrogen peroxide had been removed by evaporation. As a general rule, the substances which dissolved easily in nitrogen peroxide were also soluble in ether, although a few exceptions to this rule were noted, liquid nitrogen peroxide being usually the more powerful solvent of the two. Thus cane sugar and tartaric acid, although insoluble in ether, were both soluble in nitrogen peroxide and were unattacked by the pure solvent. As a general rule, the saturated hydrocarbons, their halogen and nitro-derivatives and the carboxylic acids, as also ketones and quinones, were stable towards this reagent, whilst the hydroxy- and amino-compounds were quickly attacked. In the case of the aromatic hydroxy-compounds which were attacked, the nitrogen peroxide brought about

a nitration, aniline derivatives were diazotised, and in some other cases simple oxidation took place. The following results will show the general behaviour of nitrogen peroxide towards organic compounds :—

(i) *Hydrocarbons.*—The unsaturated hydrocarbons have already been shown by Guthrie (*Annalen*, 1860, **116**, 248) and others to take up nitrogen peroxide. Thus amylene forms the so-called nitrosate, $NO_2 \cdot O \cdot C_5H_9 \therefore N \cdot OH$. *Benzene* and *toluene* are both miscible with nitrogen peroxide and are unacted on by it. *Naphthalene* could not be dissolved unchanged ; it was quickly attacked and gave rise to 1 : 5-dinitronaphthalene (m. p. 211°), which is also formed by the nitration of naphthalene with nitric acid. *Anthracene* was oxidised to anthraquinone, which could be easily sublimed in yellow needles melting at 273°. Pure paraffin wax, consisting of higher aliphatic hydrocarbons, appears to be unchanged by nitrogen peroxide ; it could be recovered unchanged after remaining for several days in contact with the liquid. Most specimens, however, disintegrated quickly in contact with the liquid, probably owing to reactions between the peroxide and the impurities in the paraffin.

(ii) *Nitro*-derivatives are generally very stable towards nitrogen peroxide. *Nitrobenzene*, m-*dinitrobenzene*, p-*nitrotoluene*, and 1 : 5-*dinitronaphthalene* were all easily soluble in it. The normal rise of boiling point of their solutions showed that no reaction had taken place. They were also recovered by evaporation and identified. Other nitro-derivatives are mentioned under the heading of carboxylic acids and hydroxy-compounds.

(iii) *Halogen* derivatives are also very stable. *Chloroform* and *chlorobenzene* were already known to dissolve unchanged. Besides these, we have found *ethylene dibromide*, *acetylene tetrabromide*, and *benzyl chloride* to dissolve in all proportions without reaction.

(iv) *Carboxylic Acids.*—Of these, a considerable number have been examined and have in almost every case been recovered unchanged from the solutions. In most cases, the absence of all reaction was confirmed by the electric conductivity and other methods.

Formic, *acetic*, *monochloracetic*, *trichloracetic*, *tribromacetic*, *trichlorobutyric*, *tartaric*, and *benzoic* acids were extremely easily soluble.

o-, m-, and p-*Nitrobenzoic acids*, the three *bromobenzoic* and *toluic acids*, as also *succinic* and *phthalic* acids dissolved only with difficulty.

In all these cases, the pure substances were recovered by evaporation. Slightly impure nitrogen peroxide readily attacks tartaric acid. Benzoic acid was also attacked to some extent in presence of moisture, forming a trace of *m*-nitrobenzoic acid.

(v) *Hydroxy-compounds.*—Alcohols and phenols were less stable towards nitrogen peroxide than the above-mentioned compounds.

Ethyl alcohol reacted violently with evolution of heat, forming ethyl nitrite.

Cane sugar dissolved fairly easily in nitrogen peroxide. It was not decomposed by the pure peroxide, but was quickly attacked in presence of traces of moisture.

Phenol also reacted vigorously with evolution of heat. When the liquid peroxide was added gradually to phenol, the first products of the reaction were *o*- and *p*-nitrophenol (compare Armstrong and Rossiter, Proc., 1891, 7, 92). These were, however, only intermediate products, and were completely converted into 2 : 4-dinitrophenol by excess of the peroxide; no picric acid was formed. o- and p-*Nitrophenol* were both quickly attacked and the product was in both cases the same 2 : 4-dinitrophenol.

2 : 4-*Dinitrophenol* was easily soluble in liquid nitrogen peroxide and was recovered unchanged; no picric acid was formed.

Trinitrophenol (picric acid) was very easily soluble in nitrogen peroxide and was unattacked.

Salicylic acid dissolved at first, but was quickly attacked, crystals separating out. The chief product of the reaction was 5-nitrosalicylic acid, but a small quantity of picric acid was also found in the residue.

5-*Nitrosalicylic acid* was difficultly soluble and was not attacked.

(vi) *Amines* were immediately attacked. It has been long known that gaseous nitrogen peroxide acts on aniline, forming diazobenzene nitrate (Witt, *Tagbl. Naturforscher-Vers.*, 1879, 194). Liquid nitrogen peroxide reacts with explosive violence on aniline, but the reaction proceeds more quietly when a dilute solution of nitrogen peroxide in carbon disulphide is used, and the diazo-compound separates out. The action of the liquid peroxide on substituted anilines is less violent, the diazo-compound crystallising out from the solution. In this way, o-, m-, and p-*nitraniline* and *β-naphthylamine* were converted into the corresponding diazo-compounds.

Pyridine and *quinoline* were violently attacked by liquid nitrogen peroxide, giving dark coloured products which could not be identified.

(vii) *Quinone* was easily soluble and *anthraquinone* sparingly so in the liquid peroxide, and were both unattacked by it.

II. *Electric Conductivity of Solutions in Liquid Nitrogen Peroxide.*

On account of the ease with which nitrogen peroxide can be liquefied, the measurement of the electric conductivity of its solutions presented no great difficulties. A temperature of 0° was sufficiently low to prevent any considerable evaporation of the solvent and the following experiments were all carried out at this temperature.

Measurements of the electrical resistance of pure liquefied nitrogen peroxide have already been made by Boguski (*loc. cit.*), who sealed up liquid nitrogen peroxide in tubes fitted with platinum electrodes and then determined the resistance by means of a momentary current and a galvanometer. We have confirmed his observation to the effect that the conductivity of the pure liquid is exceedingly small, but that a trace of water suffices to render it a very good conductor. Thus the addition of about 2 per cent. of water gave a solution which conducted at least as well as a $N/100$ solution of nitric acid.

Measurements of the electric conductivity of solutions of various substances in liquid nitrogen peroxide do not appear to have been made. The method used in the following experiments was the same as that usually applied to the determination of electric conductivity in aqueous solution. A Wheatstone bridge with alternating current and telephone was used. The electrodes were fixed very close to one another, so that very small conductivities could be easily measured. A cylindrical glass conductivity vessel of the usual form was used, but it was fitted with an asbestos cover, the usual wooden cover being out of the question on account of the ease with which it is attacked by the fumes. A glass stirrer was provided with which to facilitate the solution of the compounds.

In general, the nitrogen peroxide itself showed a slight but measurable conductivity, but this was due to the presence of traces of water. When no great precautions were taken to remove all traces of water, the liquid generally showed a specific conductivity of $0{\cdot}1$ to $0{\cdot}2 \times 10^{-6}$ units. The quantity of water present was too small to show itself by any green tinge in the liquid, but it could be proved that the conductivity was to be attributed to this cause by the fact that when a little phosphoric oxide was added, the conductivity gradually decreased until it became absolutely unmeasurable. We have assured ourselves that, with the apparatus used by us, a specific conductivity of $0{\cdot}02 \times 10^{-6}$ could still be detected with certainty. If we compare this with the specific conductivity of about $0{\cdot}65 \times 10^{-6}$, which is found for water which has been purified with great care (Walker and Cormack, Trans., 1900, 77, 5), we see that pure nitrogen peroxide is an almost perfect non-conductor of electricity. The following experiments will show that its solutions are likewise non-conductors. As above mentioned, the only available compounds for these conductivity measurements were acids, all bases being excluded on account of their instability, and salts on account of their insolubility, in this solvent.

A saturated solution of dry hydrogen chloride in liquid nitrogen peroxide was first examined, but showed no measurable conductivity. The following organic acids were then tested in nitrogen peroxide solution: Formic, acetic, monochloracetic, trichloracetic, trichloro-

butyric, malonic, succinic, benzoic, *o*-toluic, *m*-nitrobenzoic, phthalic, and picric acids.

Fairly concentrated solutions were employed, in most cases about 1/5 normal. These solutions were found, without exception, to be practically absolute non-conductors. It may therefore be safely concluded that substances dissolved in liquid nitrogen peroxide are not electrolytically dissociated.

III. *Molecular We ght Determinations in Liquid Nitrogen Peroxide.*

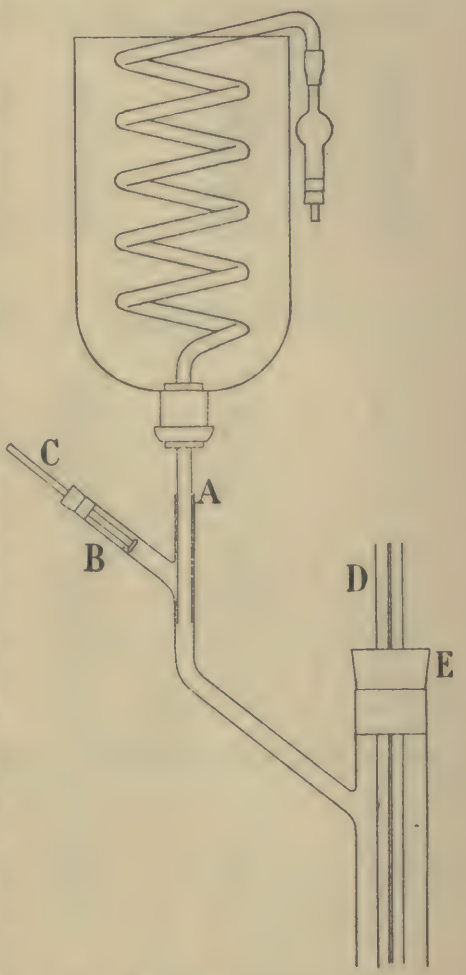
Having shown by measurements of the electric conductivity that no dissociation occurs in nitrogen peroxide solution, we thought it would be of interest to examine the state of molecular aggregation more fully by a series of molecular weight determinations.

Ramsay has already determined the lowering of the freezing point of nitrogen peroxide by a few dissolved substances (*loc. cit.*), but found the measurements difficult to carry out. Experiments on the raising of the boiling point do not appear to have been made, and this method was chosen for the following determinations. The experiments do not present any unusual difficulties; a freezing mixture of ice and salt suffices to condense the nitrogen peroxide vapour with practically no loss.

The ordinary Beckmann apparatus was employed. In the outer jacket, acetaldehyde was used, as it is naturally preferable to employ a liquid which does not attack rubber and cork. Its boiling point (20·8°) is almost the same as that of nitrogen peroxide (21·6°). The nitrogen peroxide in the inner tube was caused to boil evenly by means of glass beads and platinum foil.

The connection between the inner vessel and the spiral condenser was made as shown in the diagram (p. 1367). The condenser tube fitted loosely into the side tube of the boiling vessel, and the joint, A, was made tight by means of asbestos paper bound round with wire and coated with vaseline, the latter being frequently renewed during the experiment. In order to introduce the substance without making an open passage for the peroxide to escape into the air, the glass piston, C, was temporarily removed and the cylindrical lumps of substance, previously weighed, were introduced into the tube B. The piston, C, was then replaced and the whole condenser raised so as to make an open connection between B and the boiling vessel. By means of the rod, C, the substance was quickly pushed down so that it fell into the boiling vessel, and the condenser lowered into its original position. Thus, the escape of nitrogen peroxide during the experiment was reduced to a minimum.

The thermometer, D, was held in place by a stopper, E, made by rolling asbestos paper into a solid plug, and heating this for some time in molten paraffin wax. This was found somewhat preferable to a stopper of plaster of Paris, which was originally employed. In either case, the joints were made tight with vaseline. A number of preliminary experiments showed that the loss of liquid was inconsiderable, even when the boiling was protracted for many hours.



In order to give satisfactory results, the nitrogen peroxide must be completely freed from lower oxides by previously passing a current of oxygen through it for a considerable time at about $-10°$. After each experiment, the peroxide was recovered by distillation and the residue examined to make sure that no decomposition had occurred. In most cases, the redistilled liquid was resaturated with oxygen before being used again, as the prolonged boiling necessary in the determinations sometimes brought about a slight reaction between the solvent and the dissolved substances, by which traces of lower oxides of nitrogen were formed.

The constant for the raising of the boiling point was first ascertained with a number of indifferent substances, for which there was no likelihood of the formation of complex molecules in solution.

The following tables show the constants found for 1 gram-molecule of substance in 100 grams of solvent:

Grams of solvent.	Grams of substance.	Rise of boiling point.	Grams of substance in 100 grams of solvent.	Constant.
Nitrobenzene, $C_6H_5 \cdot NO_2$. Mol. wt. 123.				
53·6	1·012	0·215	1·89	14·0
53·6	1·591	0·317	3·01	13·1
53·6	2·352	0·464	4·39	13·0
53·6	3·108	0·612	5·80	13·0
53·6	4·227	0·841	7·89	13·1
53·6	5·569	1·105	10·39	13·1
53·6	7·250	1·457	13·52	13·2
53·6	11·792	2·394	22·00	13·4
m-*Dinitrobenzene*, $C_6H_4(NO_2)_2$. Mol. wt. 168.				
44·2	0·601	0·110	1·36	13·6
44·2	1·447	0·250	3·27	12·8
44·2	2·238	0·392	5·06	13·0
44·2	3·296	0·581	7·46	13·1
44·2	4·170	0·743	9·44	13·2
44·2	5·045	0·902	11·42	13·3
40·6	0·449	0·085	1·11	12·9
39·9	1·098	0·216	2·75	13·2
39·1	1·707	0·342	4·37	13·2
38·4	2·331	0·490	6·07	13·6
37·6	2·959	0·625	7·87	13·3
36·9	3·413	0·717	9·25	13·0
36·1	4·410	0·949	12·22	13·1
p-*Nitrotoluene*, $CH_3 \cdot C_6H_4 \cdot NO_2$. Mol. wt. 137.				
41·8	0·337	0·077	0·81	13·1
41·8	1·037	0·247	2·48	13·6
41·8	2·904	0·691	6·95	13·6
41·8	4·106	0·990	9·82	13·8
Toluene, $C_6H_5 \cdot CH_3$. Mol. wt. 92.				
49·3	1·234	0·379	2·50	13·9
49·3	2·661	0·830	5·40	14·1
49·3	3·989	1·233	8·09	14·0
49·3	5·375	1·637	10·90	13·8

Grams of solvent.	Grams of substance.	Rise of boiling point.	Grams of substance in 100 grams of solvent.	Constant.
Benzyl chloride, $C_6H_5 \cdot CH_2Cl$. Mol. wt. 126·5.				
61·0	0·750	0·139	1·23	14·3
61·0	2·538	0·476	4·16	14·5
61·0	3·558	0·662	5·83	14·4
61·0	4·944	0·916	8·11	14·3
61·0	7·052	1·289	11·56	14·1
61·0	9·010	1·627	14·78	13·9
61·0	10·811	1·926	17·72	13·8
Acetylene tetrabromide, $C_2H_2Br_4$. Mol. wt. 346.				
52·6	1·336	0.101	2·54	13·8
52·6	4·190	0·340	7·97	14·8
52·6	7·663	0·607	14·57	14·4
52·6	9·915	0·743	18·85	13·6
Ethylene dibromide, $C_2H_4Br_2$. Mol. wt. 188.				
50·9	0·880	0·134	1·73	14·6
50·9	2·487	0·387	4·89	14·9
50·9	3·976	0·620	7·81	14·9
50·9	5·340	0·824	10·49	14·8
50·9	7·417	1·102	14·57	14·2
50·9	11·575	1·650	22·75	13·6
50·9	15·503	2·127	30·45	13·1
Quinone, $O{:}C_6H_4{:}O$. Mol. wt. 108.				
46·5	0·687	0·181	1·48	13·2
46·5	1·199	0·328	2·58	13·7
46·5	1·675	0·462	3·60	13·9
Acetophenone, $C_6H_5 \cdot CO \cdot CH_3$. Mol. wt. 120.				
59·8	1·902	0·345	3·18	13·0
59·8	2·741	0·524	4·58	13·7
59·8	3·972	0·768	6·64	13·9
59·8	5·094	0·987	8·52	13·9
59·8	6·161	1·195	10·30	13·9

The following is a list of the mean constants found in the above experiments:

Substance.	Mean constant.
Nitrobenzene	13·2
Dinitrobenzene (1st series)	13·2
„ (2nd series)	13·2
p-Nitrotoluene	13·5
Toluene	14·0
Benzyl chloride	14·2
Acetylene tetrabromide	14·2
Ethylene dibromide	14·3
Quinone	13·6
Acetophenone	13·7
Mean	13·7

The fifty-five observations comprised in these ten series rarely deviated by more than 5 per cent. from this mean value. The number 13·7 may therefore be safely concluded to be a close approximation to the constant for 1 gram-molecule of substance dissolved in 100 grams of liquid nitrogen peroxide.

Our attention was next turned to the examination of the acids the electric conductivity of which we had previously investigated. The results of our experiments show that many acids are *associated* in nitrogen peroxide solution and exist in the form of double molecules. Association is well known to take place in certain other solvents (benzene, &c.).

At the lowest concentration taken, namely, 2·45 per cent., benzoic acid was not quite completely associated to double molecules. At a concentration of 5 per cent., however, the association was practically complete and remained nearly constant at the higher concentrations.

Benzoic Acid.

$C_6H_5 \cdot CO_2H$; mol. wt. 122. $(C_6H_5 \cdot CO_2H)_2$; mol. wt. 244.

Weight of solvent in grams.	Weight of substance in grams.	Rise in boiling point.	Grams of substance in 100 grams of solvent.	Molecular weight (found).
42·9	1·049	0·160	2·45	209
42·9	2·048	0·277	4·77	236
42·9	2·952	0·411	6·88	229
42·9	3·973	0·556	9·26	228

In dealing with the substituted benzoic acids, we were met with the difficulty that most of the acids in question were sparingly soluble in nitrogen peroxide, as in other solvents. Even at the highest concentration taken, the association to double molecules was incomplete. It will be seen, nevertheless, from the following figures that the acids are strongly associated and we may assume that they would exist in the form of double molecules in more concentrated solutions. *o*-Toluic acid was the most easily soluble of those tried, but its association was still somewhat incomplete at the highest concentrations employed.

Toluic Acids.

$CH_3 \cdot C_6H_4 \cdot CO_2H$; mol. wt. 136. $(CH_3 \cdot C_6H_4 \cdot CO_2H)_2$; mol. wt. 272.

Weight of solvent in grams.	Weight of substance in grams.	Rise in boiling point.	Grams of substance in 100 grams of solvent.	Molecular weight (found).
		o-*Toluic acid.*		
51·0	0·223	0·030	0·44	200
51·0	0·723	0·086	1·42	226
51·0	1·277	0·141	2·50	243
51·0	1·869	0·211	3·66	238
51·0	2·450	0·279	4·80	236
51·0	3·189	0·353	6·25	243
51·0	4·176	0·463	8·19	242
		m-*Toluic acid.*		
51·0	0·265	0·036	0·52	198
51·0	0·712	0·085	1·40	225
51·0	1·013	0·120	1·99	227
51·0	1·362	0·160	2·67	229
		p-*Toluic acid.*		
57·8	0·581	0·071	1·01	194
57·8	1·074	0·129	1·86	197

Experiments with the nitrobenzoic acids failed to give satisfactory values, the acids being very sparingly soluble in nitrogen peroxide. The measurements taken in dilute solution pointed, however, to a considerable association. Experiments were also commenced with the bromobenzoic acids, but were discontinued for the same reason.

A similar association was found for the acids of the aliphatic series.

For acetic acid, only the first of a series of measurements is given, the others having been rendered inaccurate by a slight decomposition which the nitrogen peroxide underwent. It is sufficient to show that a complete association to double molecules had taken place.

Weight of solvent in grams.	Weight of substance in grams.	Rise in boiling point.	Grams of substance in 100 grams of solvent.	Molecular weight (found).
		Acetic Acid.		
$CH_3 \cdot CO_2H$; mol. wt. 60.			$(CH_3 \cdot CO_2H)_2$; mol. wt. 120.	
57·8	1·608	0·313	2·78	122
		Tribromacetic Acid.		
$CBr_3 \cdot CO_2H$; mol. wt. 297.			$(CBr_3 \cdot CO_2H)_2$; mol. wt. 594.	
55·9	0·518	0·023	0·93	552
55·9	1·192	0·051	2·13	573
55·9	2·126	0·086	3·80	606
		Trichlorobutyric Acid.		
$C_3H_4Cl_3 \cdot CO_2H$; mol. wt. 191·5.			$(C_3H_4Cl_3 \cdot CO_2H)_2$; mol. wt. 383.	
54·5	0·464	0·050	0·85	233
54·5	0·839	0·085	1·54	248
54·5	1·378	0·133	2·53	260
54·5	1·943	0·185	3·57	264
54·5	2·602	0·245	4·77	267
54·5	3·350	0·308	6·15	273
54·5	3·797	0·340	6·97	281

The association will be seen to be much less complete in the case of trichlorobutyric acid.

Since acids showed a tendency to form complex molecules in nitrogen peroxide, an examination of the phenols seemed desirable. As mentioned above, most phenols are readily attacked by nitrogen peroxide. The choice of available phenols was therefore limited. In the following cases, the normal molecular weights were found :

Weight of solvent in grams.	Weight of substance in grams.	Rise in boiling point.	Grams of substance in 100 grams of solvent.	Molecular weight (found).
2 : 4-*Dinitrophenol*, $OH \cdot C_6H_3(NO_2)_2$. Mol. wt. 184.				
49·3	0·227	0·034	0·46	186
49·3	0·480	0·074	0·97	180
49·3	0·862	0·135	1·75	177
2 : 4 : 6-*Trinitrophenol*, $OH \cdot C_6H_2(NO_2)_3$. Mol. wt. 229.				
41·0	0·939	0·143	2·29	219
40·4	1·675	0·243	4·15	234
39·8	2·405	0·350	6·04	237
39·3	3·151	0·448	8·02	245
38·7	4·061	0·559	10·50	257

IV. *Summary of Results.*

1. Nitrogen peroxide does not dissolve inorganic salts. On the other hand, it is a good solvent for certain non-metallic elements and readily dissolves many organic compounds.

2. The perfectly anhydrous liquid is comparatively inert as a chemical reagent; many organic compounds can be recovered unchanged from their solutions in nitric peroxide.

3. Measurements of the electric conductivity show that it is not an "ionising solvent."

4. Molecular weight determinations show that many substances are associated to double molecules in this solvent.

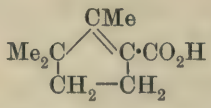
University of Birmingham.

CXLV.—*The Action of Aluminium Chloride on Camphoric Anhydride. Part II.*

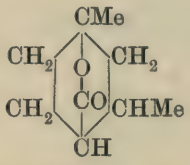
By W. H. Perkin, jun., and J. Yates.

In the first part of this paper, published a short time ago (Lees and Perkin, this vol., 332), it was shown that when camphoric anhydride, dissolved in chloroform, is treated in the cold with aluminium chloride, the camphor molecule undergoes a series of remarkable molecular changes.

The substances formed during this decomposition and described in the first paper were *iso*lauronolic acid,

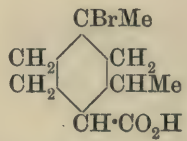


and a mixture of isomeric lactones, which, since they are readily converted into xylic acid on oxidation with sulphuric acid, were recognised as stereoisomeric modifications of the lactone of hydroxyhexahydro-xylic acid,



By hydrolysing the mixed lactones we succeeded, in a way described in detail in that paper, in isolating two well characterised stable hydroxyhexahydro-xylic acids melting at 160° and 113° respectively, which we called simply A and B, since we had no means of determining their configurations. When distilled, these acids were converted into the corresponding lactones with elimination of water, the lactone of the A-acid melted at 55°,* and that of the B-acid at 44°.

We have since further examined these two hydroxy-acids and their lactones and find that the A-acid or its lactone, when treated with fuming hydrobromic acid, is converted into *A-bromohexahydro-xylic acid*,



which melts at 133°, whereas the B-hydroxy-acid and its lactone, under similar conditions, yield *B-bromohexahydro-xylic acid* melting at 126°.

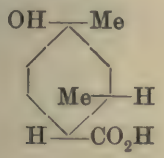
In our earlier experiments, several results were obtained which seemed to indicate that the lactone mixture obtained by the action of aluminium chloride on camphoric anhydride did not consist entirely of the two lactones of A- and B-hydroxyhexahydro-xylic acid, but contained other isomeric lactones, which we were at that time unable to isolate. Since then, by experimenting with large quantities of material, this

* This lactone was described as an oil, but it subsequently solidified.

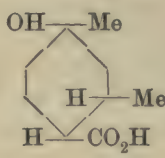
suspicion has been confirmed and we have now been able to identify all the constituents of the mixture.

The two hydroxy-acids, A and B, are characterised by remarkable stability, since, although they contain the hydroxyl and carboxyl groups in the δ-position, they are not converted into their lactones even by prolonged boiling with water, and it was found necessary, in order to prepare these lactones, to submit the acids to dry distillation.*

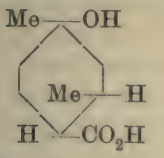
In order to explain this remarkable stability, we suggested in the earlier paper that the two hydroxy-acids, A and B, were probably the *trans*-modifications,



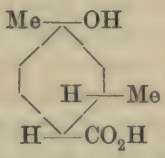
and



The corresponding *cis*-modifications,

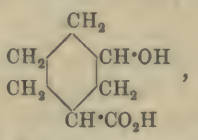


and

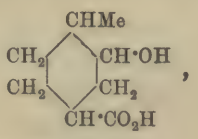


might be expected to exhibit much less stability, and be converted into their lactones when their salts are acidified, as is the case with the δ-hydroxy-acids in the fatty series.

* Somewhat similar cases of stable ring hydroxy-acids have already been observed. Thus, the hydroxy*cyclo*hexanecarboxylic acid of the formula



which Einhorn (*Annalen*, 1896, **291**, 298) prepared by reducing *m*-hydroxybenzoic acid, is quite stable although it is a γ-hydroxy-acid. Again, Tiemann and Semmler (*Ber.*, 1895, **28**, 2143) describe as stable the γ-hydroxyhexahydro-*p*-toluic acid of the formula:



Both these acids are probably *trans*-modifications.

The existence of *cis*- and *trans*-isomerism in the case of ring-acids containing the

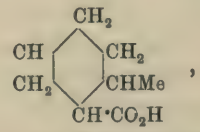
By making use of these differences in stability we have now succeeded in showing that the mixed lactones obtained by the action of aluminium chloride on camphoric anhydride contain, not only the lactones of the *trans*-A- and B-hydroxyhexahydro-xylic acids, but also the corresponding *cis*-lactones. The process employed in separating the latter is briefly as follows:

The mixed lactones are first converted into the hydroxy-acids by hydrolysis and these then submitted to distillation in steam; in this way, the *cis*-hydroxy-acids are converted into lactones which pass over with the steam, whereas the *trans*-acids remain for the most part unchanged in the distilling flask, so that by repeating this process an almost complete separation is possible. The last traces of *trans*-acids are removed by hydrolysing the lactones and allowing the hydroxy-acids to stand for a few days, when the *cis*-modifications are spontaneously converted into lactones, which are separated from any traces of *trans*-hydroxy-acids by treatment with sodium carbonate. In this way, more than 100 grams of oil were obtained, which distilled constantly at 145° under 25 mm. pressure, and, like the *trans*-lactones, yielded xylic acid when treated with sulphuric acid; there can therefore be no doubt that it consisted of the *cis*-lactones of hydroxyhexahydro-xylic acid.

Further examination showed that this oil contains two lactones (one, however, only in extremely small quantity), since when treated with fuming hydrobromic acid the oil yields a solid product which, when crystallised from light petroleum, may be separated into a small quantity of a very sparingly soluble C-bromohexahydro-xylic acid melting at 137° and a large quantity of the more soluble D-bromohexahydro-xylic acid, which melts at 130°. At first it was thought that the two bromo-acids, A and C, melting at 133° and 137°, and the two B, and D, melting at 128° and 130° were identical, but investigation showed that this is not the case.

If, for example, the first two are intimately mixed, the mixture melts at about 100° and a mixture of the two latter was found to melt at about 105°, and again, the four bromo-acids differ in their behaviour with sodium carbonate: a point which will be discussed at a later stage.

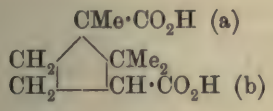
groups CHMe and $CH{\cdot}CO_2H$ has already been observed. Thus, hexahydro-*o*-toluic acid,



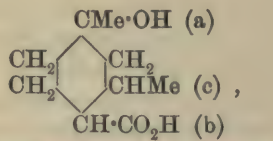
exists in well-defined *cis*- and *trans*-modifications (Goodwin and Perkin, Trans., 1895, **67**, 121).

It is therefore evident that there are four distinct bromo-acids, $C_9H_{15}O_2Br$, two *cis* and two *trans*, and this agrees with the assumption that the hydroxy-acids, $C_9H_{15}O_2{\cdot}OH$, from which they are derived, are stereoisomeric modifications of hydroxyhexahydro-xylic acid, and that the bromo-acids are therefore stereoisomeric bromohexahydro-xylic acids: this will be evident from the following considerations.

If the formula of camphoric acid is compared with that of hydroxyhexahydro-xylic acid,



Camphoric acid.



Hydroxyhexahydro-xylic acid.

it will be seen that not only are the two asymmetric carbon atoms in the camphoric acid (marked a, b) present in the hydroxyhexahydro-xylic acid, although in a somewhat altered form, but that in the formation of the latter acid from the former a new asymmetric carbon (marked c) has been created: in other words, hydroxyhexahydro-xylic acid contains *three* asymmetric carbon atoms. In order to discuss this point, we may conveniently select the four bromo-acids A, B, C, and D, and it may be stated at once that experiment has shown that these are all inactive and that, therefore, racemisation must have taken place in their formation from the strongly dextrorotatory camphoric anhydride. In the case of a substance containing three asymmetric carbon atoms, a, b, c, the possible combinations, using the signs + and − are:

+ a − a	+ a − a	+ a − a	− a + a
+ c − c	− c + c	− c + c	− c + c
+ b − b	+ b − b	− b + b	+ b − b
1 2	3 4	5 6	7 8

that is to say, there are four possible externally compensated combinations, 1 : 2, 3 : 4, 5 : 6, and 7 : 8, and it is highly probable that the four bromo-acids, A, B, C, and D, and their corresponding hydroxy-acids, are these combinations. Unfortunately, it is not possible at this stage to assign to *each* modification its particular configuration. We may, however, select the combination [+a−c−b, −a+c+b] for C, in which case D will be [−a−c+b, +a+c−b], and the acids A and B will be represented by [+a+c+b, −a−c−b] and [+a−c+b, −a+c−b], but which of these symbols belongs to A, and which to B, must be left an open question.

In connection with this question of the introduction of a new asymmetric carbon atom into a molecule containing already one or more such carbon atoms, we may perhaps be allowed to call attention to the

following very interesting aspect of the subject, since it arises directly from our experimental work.

It has already been stated that the results briefly described above leave little room for doubting that during the conversion of *d*-camphoric acid the change proceeds in such a way as to yield the four externally compensated hydroxyhexahydro-xylic acids, to which only the configurations given on page 1377 can be assigned. It thus follows that the camphor residue has, during the treatment with aluminium chloride, undergone racemisation in a manner similar to, although probably more complete than, that observed by Kipping and Pope (Trans., 1897, 71, 956) to occur on sulphonating camphor; and whilst in the latter case the complex $+a+b$ became converted into $-a-b$, in the case now described the other two complexes, $+a-b$ and $-a+b$, are also produced at some stage during the series of reactions. The formation of a third asymmetric carbon atom in addition to the two already present results in the ultimate production of all eight possible configurations of the substance containing three dissimilar asymmetric carbon atoms.

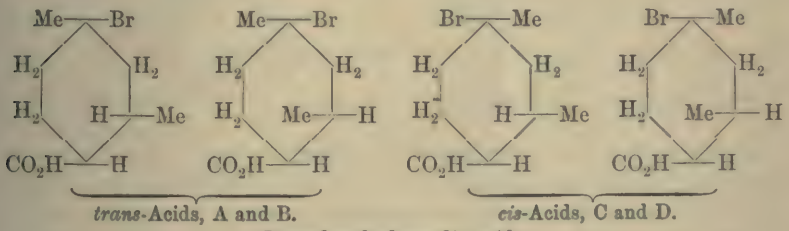
Quite recently (Cohen and Whiteley, Proc., 1900, 16, 212; Kipping, *ibid.*, 226), the question has again been opened as to whether in converting an optically active substance containing *n*-asymmetric carbon atoms into one containing $n+1$ such atoms, the configuration of the *n*-asymmetric carbon atoms originally present exercises a directive influence on the configuration of the new asymmetric carbon atom. This question seems to have been answered in the affirmative by Fischer's work, and more especially by his observation that *d*-mannose, which contains four asymmetric carbon atoms, gives an almost quantitative yield of *d*-mannoheptonic acid (*Ber.*, 1889, 22, 370), which contains five asymmetric carbon atoms in the molecule. A number of well-known facts leading to the same conclusion are available and the work now described also points in the same direction. Thus, it is well known that on brominating succinic acid two optically inactive dibromosuccinic acids are obtained in different quantities, the isomeride (*iso*dibromosuccinic acid) produced in much the smaller amount having the configuration $[+a+a,-a-a]$, whilst ordinary dibromosuccinic acid is the internally compensated compound having the configuration $[+a-a]$. Since monobromosuccinic acid containing one asymmetric carbon atom is first produced and on further bromination yields more internally than externally compensated dibromosuccinic acid, it follows that the presence of one asymmetric carbon atom in this case causes the second to assume, by preference, the opposite configuration to the first. The literature concerning the tartaric acids reveals similarly convincing proofs of the same proposition. The possibility of drawing, from the behaviour of optically

inactive substances, sound conclusions as to the directive influence exerted by the configuration of asymmetric carbon atoms already existent in the substance upon that of others ultimately produced, seems hitherto to have been overlooked. In the formation of the hydroxyhexahydro-xylic acids with three asymmetric carbon atoms from camphoric acid containing only two, we show that the four externally compensated isomerides produced are formed in widely different proportions, which may be roughly stated to be as follows: A, 12 per cent.; B, 5 per cent.; C, 3 per cent.; D, 80 per cent. Although we are unable at present to definitely distribute the four pairs of possible configurations amongst these four acids, the fact that these acids are formed in different quantities is convincing proof that the configurations of the two original asymmetric carbon atoms have exercised a directive influence on the configuration of the carbon atom, which becomes asymmetric during the action of the aluminium chloride.

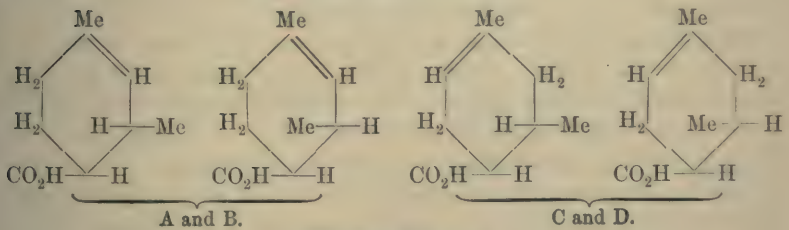
When the four bromo-acids, A, B, C, D, are boiled with sodium carbonate, they are all decomposed with elimination of hydrogen bromide and formation of tetrahydro-xylic acids,

$$C_9H_{15}O_2Br = C_9H_{14}O_2 + HBr,$$

and according to theory, four different externally compensated acids should be formed in this way, as will be seen at once if the bromo-acids are represented graphically and the corresponding tetrahydro-xylic acids written underneath.



Bromohexahydro-xylic acids.



Tetrahydro-xylic acids.

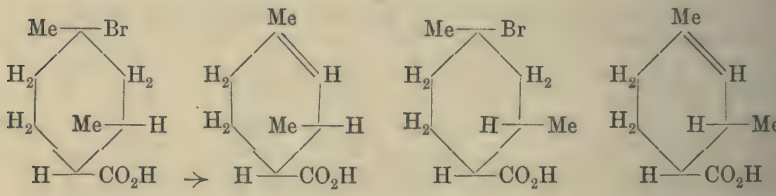
As in this change (elimination of hydrogen bromide), only one of

the three asymmetric carbon atoms in the bromohexahydro-xylic acids disappears, each of the unsaturated acids formulated above still contains two asymmetric carbon atoms and is an externally compensated compound; the optical relationship of these four racemic compounds may therefore be expressed by the same signs as before, omitting that given to the >CMeBr-group. The tetrahydro-xylic acid, C, will therefore be [−c−b, +c+b], D will be [−c+b, +c−b], and A and B will be either [+c+b, −c−b] or [−c+b, +c−b].

The actual results of the experiments on the behaviour of the four bromo-acids with sodium carbonate show that the three bromo-acids, A, B, and D, give three distinct tetrahydro-xylic acids, A, B, and D, which melt at 80°, 68°, and 87° respectively, but in the case of the bromo-acid, C, the material at our disposal was so small that we were unable to purify the acid formed sufficiently to determine its melting point accurately; most probably it is the fourth isomeride indicated by theory.

There is, however, at present no proof of the actual position of the double linkings in the tetrahydro-xylic acids, and the formulæ given above are only intended as examples of the direction in which elimination of hydrogen bromide may possibly take place.

It is clear that the relationship, for example, between the *cis*-bromo-acids, C and D, and their corresponding tetrahydro-xylic acids might equally well be written thus:

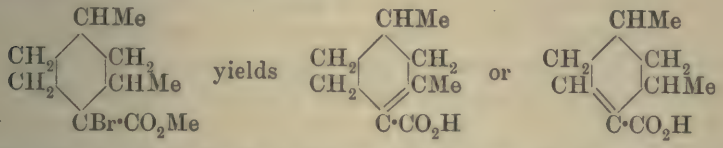


In order, if possible, to obtain some clue as to the constitution of these unsaturated acids, experiments (see pp. 1388, 1393) were instituted on the oxidation of the tetrahydro-xylic acids, A and D, but the results obtained with the small quantities of these acids available were not sufficient to throw much light on this point.

When treated with fuming hydrobromic acid, the three tetrahydro-xylic acids A, B, and D are quantitatively reconverted into the bromo-acids from which they were derived by elimination of hydrogen bromide, the bromine atom becoming attached in each case, therefore, to the tertiary carbon atom carrying the methyl group.

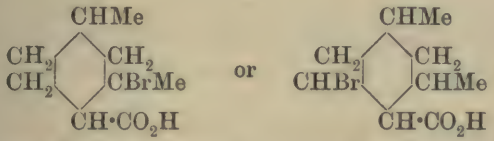
Another characteristic of these acids is that when warmed with sulphuric acid at 80° they are rapidly oxidised to xylic acid and, indeed, this change takes place at the ordinary temperature if the solution in sulphuric acid is allowed to stand for some days.

During the course of a series of experiments on the reduction of xylic acid by means of sodium and *iso*amyl alcohol, Bentley and Perkin (Trans., 1897, 71, 173) obtained a tetrahydro-xylic acid which melts at 107° and is isomeric with the tetrahydro-xylic acids, A, B, and D, described in the present paper. That this acid is either Δ^1- or Δ^6-tetrahydro-xylic acid is conclusively proved by the fact that it is formed from methyl α-bromohexahydro-xylate by hydrolysis and elimination of hydrogen bromide.



In order to obtain further evidence in support of the assumption that the acids A, B, and D are tetrahydro-xylic acids, we decided to further examine this acid of melting point 106°, and as the result of our experiments we find in properties and behaviour with reagents it shows a quite striking similarity to the acids A, B, and D.

Thus, for example, when heated with sulphuric acid, it is readily oxidised to xylic acid, and it combines readily with hydrogen bromide, yielding a new bromohexahydro-xylic acid which melts at 127° and the constitution of which is doubtless represented by one of the formulæ,



It is remarkable that the five bromohexahydro-xylic acids described in this paper should all melt between 127° and 137°, and that the three tetrahydro-xylic acids, A, B, and D, should all melt close together and be so very similar in properties. The impossibility of readily distinguishing between these different isomeric modifications has very greatly added to the difficulties of this reseach.

Experimental.

Separation of the Lactones produced by the action of Aluminium Chloride on Camphoric Anhydride.

In the introduction, it was stated that a new method for separating these lactones had been worked out, which gives much more satisfactory results than that described in the previous paper and is especially convenient for the rapid isolation of the *cis*-lactones. This method is as follows:

The solution of the camphoric anhydride in chloroform is first treated with aluminium chloride exactly as described in the previous paper, and after separating the *iso*lauronolic acid by means of potash, the chloroform solution of the lactones is distilled from the water-bath until as much chloroform as possible has been removed. The dark-brown residue, which often still contains 50 per cent. of its weight of chloroform, is fractionated twice under reduced pressure, when the whole passes over at 170—180° (80 mm.) as a colourless oil, the weight of which from 1 kilo. of camphoric anhydride is usually about 130 grams. The mixed lactones from 2 kilos. of camphoric anhydride were now treated on the water-bath with sufficient moderately concentrated barium hydroxide to just dissolve them, the solution filtered from a small quantity of a dark-coloured impurity, the filtrate acidified, saturated with calcium chloride, and extracted at least 20 times with pure ether. The ethereal solution was then evaporated and the residual thick oil submitted to distillation in a rapid current of steam (*a*). When oil ceased to come over with the condensed water, the distillate was saturated with ammonium sulphate, repeatedly extracted with ether, and after evaporating off the ether, the oily lactone mixture was again boiled with barium hydroxide until dissolved: the solution was then cooled to 60°, acidified with excess of hydrochloric acid, and kept at 60° for 5 minutes.

After saturating with calcium chloride, the whole was extracted twenty times with ether; the ethereal solution was then well washed with strong sodium carbonate (*b*), dried over calcium chloride, evaporated, and the residual colourless oil distilled under reduced pressure.

During the first distillation, the whole quantity passed over at 174—177° (80 mm.) and weighed 120 grams; on distilling again, more than 100 grams passed over between 175° and 176° under the same pressure. On analysis:

0·1176 gave 0·3017 CO_2 and 0·099 H_2O. C = 70·0; H = 9·3.

$C_9H_{14}O_2$ requires C = 70·1; H = 9·1 per cent.

This lactone was slightly lævorotatory, the observed rotation in a 100 mm. tube being only −4·24°.

In order to make quite sure that this oil was quite free from even traces of the lactones of the *trans*-acids A and B, it was again dissolved in baryta water, and the solution, after standing until quite cold, acidified with excess of hydrochloric acid, care being taken that the temperature did not rise above 15°. The whole was then allowed to stand for 24 hours, when it was noticed that the oily layer, which at first was quite thick, had become much more mobile. After extracting as usual with ether, the ethereal solution was washed repeatedly with

sodium carbonate (*c*), dried over calcium chloride, and evaporated, when 90 grams of a lactone were obtained which distilled constantly at 145° under 25 mm., and at 255° under 760 mm. pressure, and had a rotation in a 100 mm. tube of −5·3°. Experiment showed that further treatment with baryta, exactly as just described, did not alter this rotation or the other physical constants of the oil. It was therefore clear that it was now quite free from the lactones of the *trans*-A- and B-acids, and consisted of the lactones of the *cis*-acids only. In this condition, it was employed in the experiments described in this paper. On analysis, the following numbers were obtained :

0·1646 gave 0·4237 CO_2 and 0·1376 H_2O. C = 70·2 ; H = 9·3.
$C_9H_{14}O_2$ requires C = 70·1 ; H = 9·1 per cent.

The density and magnetic rotation of this oil were determined by W. H. Perkin, sen., with the following results :

Density determinations: *d* 10°/10° = 1·0503 ; *d* 15°/15° = 1·0471 ; *d* 20°/20° = 1·0441.

Magnetic rotation.

t.	Sp. rotation.	Mol. rotation.
15°	1·0562	8·632

These numbers differ considerably from the previous determinations made with the mixture of *cis*- and *trans*-lactones, the density was then at 10°/10° = 1·0606 and the magnetic rotation 8·200, and they naturally differ still more for the values found for the lactone of the *trans*-acid A (see p. 1390), which are as follows : Density, *d* 10°/10° = 1·0640 ; magnetic rotation, 8·174.

Action of Sulphuric Acid on the cis-*Lactones. Formation of Xylic Acid.*—The oily lactone just described dissolves in concentrated sulphuric acid with development of a good deal of heat, and if the solution is heated at 80° it rapidly darkens and much sulphur dioxide is evolved. After heating for 15 minutes, the product was poured into water and allowed to stand overnight ; the dark precipitate was then collected, dissolved in sodium carbonate, and boiled with purified animal charcoal. On acidifying, a rather dark coloured crystalline mass separated, and this, after drying, was distilled and the distillate crystallised from dilute acetic acid, when almost colourless crystals separated which melted at 124—125° and consisted of *xylic acid*, $C_6H_3(CH_3)_2 \cdot CO_2H$. On analysis :

0·1298 gave 0·3422 CO_2 and 0·0794 H_2O. C = 71·9 ; H = 6·8.
$C_9H_{10}O_2$ requires C = 72·0 ; H = 6·7 per cent.

Separation of the Substances Removed during the Purification of the cis-*Lactones.*

During the purification of the *cis*-lactones, as described in the previous section, more than half of the original mixture of *cis*- and *trans*-lactones was removed during the steam distillation and afterwards by the repeated extractions with sodium carbonate. The investigation of this material was carried out briefly as follows. The sodium carbonate extract *b* (p. 1382) was acidified, saturated with calcium chloride, and repeatedly extracted with ether; the ethereal solution, after carefully drying over calcium chloride and evaporating to a small bulk, yielded, on standing, 17 grams of colourless crystals, which, after recrystallisation from ether, melted at 158—160° and consisted of pure A-hydroxyhexahydro-xylic acid (this vol., p. 345).

The ethereal mother liquors of these crystals deposited, on spontaneous evaporation, several crops of crystals which, when left in contact with porous porcelain to remove oily impurity, became hard and colourless, and on subsequently recrystallising from ether, yielded further quantities of the A-acid.

The total amount of pure A-acid obtained from this sodium carbonate extract was 27 grams.

It is rather remarkable that such considerable quantities of the A-acid should be found at this place, since its presence here shows that it must have been carried over during the steam distillation, yet in the previous paper (p. 345) it was shown that the pure A-acid is not volatile as such with steam, nor is it converted into its volatile lactone under these conditions. It therefore follows that in the present case its volatility must be due to the presence of the lactones of the *cis*-acids, which carry it over during the steam distillation.

The sodium carbonate extract *c* (p. 1383) was acidified with excess of hydrochloric acid, when a thick, heavy oil separated, which on standing at the ordinary temperature for 3 weeks became much less dense and more mobile. The whole was then saturated with calcium chloride, repeatedly extracted with ether, the ethereal solution washed well with strong sodium carbonate (*d*), dried over calcium chloride, and evaporated. In this way, about 80 grams of an oil were obtained which distilled constantly at 163° (40 mm.), and had a rotation of $-4{\cdot}4°$ in a 100 mm. tube. This was further purified by solution in baryta water and treatment with hydrochloric acid at the ordinary temperature, as previously described in purifying the main bulk of the *cis*-lactones (p. 1382); it then yielded more than 70 grams of pure *cis*-lactones. Thus, without allowing for considerable loss during purification, the total yield of the *cis*-lactones from 250 grams of the mixed lactones

is at least 170 grams. The sodium carbonate extract *d* was treated in exactly the same way as *c*, and yielded small quantities of the *cis*-lactones and about 0·5 gram of pure crystalline A-acid.

The steam distillation flask, *a*, contained a considerable quantity of a thick oil; this was repeatedly extracted with ether and after drying the ethereal solution and evaporating, the residual oil was several times carefully distilled. During the first distillation, much water was given off and a colourless oil was collected at 160—170° under 35 mm. pressure, leaving in the flask a slight crystalline residue of camphoric anhydride which had escaped the action of the aluminium chloride. In order to remove this as far as possible, the oil was carefully dried and several times slowly fractionated under 35 mm. pressure, when almost the whole passed over at 155—160°.

When this oil was dissolved in baryta water and, after acidifying, the acids extracted with ether, an oil was obtained which, even after standing for months, deposited only a very few crystals; it was therefore distilled under the ordinary pressure, when almost the whole quantity came over at 252—255° (750 mm.) The distillate was dissolved in ether and repeatedly extracted with dilute potash, and the alkaline solution, after freeing from ether, was acidified, when a considerable quantity of an oil was precipitated which, on standing, became semi-solid.

In contact with a porous plate, the oily impurity was soon absorbed and a crystalline mass resulted, which after crystallising from dilute acetic acid melted at 78—80° and consisted of A-tetrahydro-xylic acid (p. 1392).

0·1481 gave 0·3802 CO_2 and 0·1224 H_2O. C = 70·0; H = 9·2.
$C_9H_{14}O_2$ requires C = 70·1; H = 9·1 per cent.

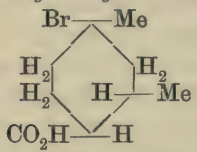
This acid, which weighed about 3 grams, is undoubtedly formed by the elimination of water from A-hydroxyhexahydro-xylic acid, during the frequent distillations, since it is elsewhere proved (p. 1391) that small quantities of A-tetrahydro-xylic acid are always produced when the A-hydroxy-acid is distilled. The ethereal solution which had been separated from the alkaline extract, gave, on evaporation, a colourless oil, and this was converted into the hydroxy-acid by treatment with baryta in the usual way.

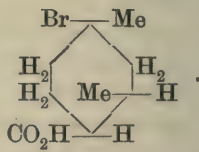
On long standing, the thick, oily acid partially crystallised and when spread on a porous plate a colourless mass of crystals was obtained, which, after recrystallisation from ether, melted at 158—160° and consisted of A-hydroxyhexahydro-xylic acid. The porous plate was broken up and extracted in a Soxhlet apparatus with ether, and the ethereal extract, after a long series of fractional crystallisations, yielded about 2 grams of A-hydroxy-acid and 5 grams of pure B-hydroxy-

hexahydro-xylic acid, which melted at 113° and on distillation was decomposed with elimination of water and formation of the pure B-lactone melting at 44°.

It is remarkable that so little of the B-acid should have been obtained on this occasion, because in the previous experiments (*loc. cit.*, p. 346), a relatively large quantity of it could always be isolated with comparative ease. This great difference in yield proves that the relative quantity of the lactones formed by the action of aluminium chloride on camphoric anhydride varies with unavoidable slight alterations in the conditions of the experiment.

Action of Hydrobromic Acid on the cis-*Lactones of Hydroxyhexahydro-xylic Acid. Formation of the* cis-*Modifications* (C and D) *of Bromohexahydro-xylic Acid,*





When the mixed *cis*-lactones, in quantities of not more than 5 grams are rapidly mixed with four times the volume of fuming hydrobromic acid (saturated at 0°), they rapidly and completely dissolve, but in a few seconds the solution becomes opaque owing to the separation of oil. The oil collects as a clear layer on the surface of the acid and after standing for 24 hours solidifies to a colourless, crystalline mass. This is powdered, washed with water on the pump, and left in contact with porous porcelain until quite dry; it is then ground up with light petroleum (b. p. 35—40°), in which it is very sparingly soluble, and washed with this solvent on the pump. The latter operation not only removes traces of coloured impurity but dissolves a small quantity of unchanged lactone, which always appears to be present, even when a large excess of hydrobromic acid is used. The colourless residue is *rapidly** dissolved in boiling light petroleum (b. p. 80—90°), a pinch of purified animal charcoal added, the liquid filtered, and carefully watched as it crystallises. A small crop of prismatic crystals of the C-bromo-acid quickly forms, then there is a pause in the crystallisation, and if the liquid is quickly poured off and well stirred, a mass of needles of the D-bromo-acid rapidly separates. By repeating this operation, it is quite easy to completely separate these two acids.

C-Bromohexahydro-xylic Acid crystallises in glistening, prismatic needles and melts at about 137—138° if the determination is rapidly

* Unless this operation is very rapidly performed, the bromo-acids decompose with evolution of quantities of hydrogen bromide.

carried out, but as it decomposes on heating with evolution of hydrogen bromide, a considerably lower melting point will be observed if the operation is conducted slowly. On analysis:

0·2108 gave 0·1697 AgBr. Br = 34·2

$C_9H_{15}O_2Br$ requires Br = 34·0 per cent.

This C-bromo-acid is very sparingly soluble in light petroleum and so similar in its other properties to A-bromohexahydro-xylic acid (m. p. 133°, p. 1391) that it was at first thought that the two were identical. Carefully purified specimens of each of these two acids were therefore intimately mixed, and it was then found that the melting point of the mixture was about 100—105°, a conclusive proof that the two bromo-acids C and A are not identical.

So far as could be seen with the small quantity of material at our disposal (2 grams dissolved in 100 c.c. of pure ether), C-bromohexahydro-xylic acid is inactive; in dissolves readily in sodium carbonate, and on acidifying the solution and heating to boiling, some of the tetrahydro-xylic acid formed appears to be converted into the C-lactone; if this is removed by making alkaline with sodium carbonate and extracting with ether and the alkaline solution acidified, an oil separates which solidifies on standing and probably consists of C-tetrahydro-xylic acid. From this small experiment, the C-bromo-acid appears to behave somewhat differently from the A-, B-, and D-bromo-acids, which do not yield lactones when treated in this way. This difference, however, requires confirmation before it can be definitely accepted.

The *D-bromohexahydro-xylic acid*, after complete separation from the C-acid by repeated recrystallisation from light petroleum, melts at about 128—130° and separates from light petroleum, in which it is sparingly soluble in the cold, as a voluminous mass of needles, which completely fill the liquid. It is readily soluble in ether and a solution in this solvent containing 5 grams in 100 c.c. was found, on examination, to be quite inactive.

It dissolves readily in dilute sodium carbonate, and on boiling the solution elimination of hydrogen bromide takes place with formation of *D-tetrahydro-xylic acid* (see next section). An analysis of D-bromohexahydro-xylic acid yielded the following results:

0·1896 gave 0·1514 AgBr. Br = 34·1.

$C_9H_{15}O_2Br$ requires Br = 34·0 per cent.

It may, at first sight, seem remarkable that the bromo-acids C and D should show no signs of activity, although the *cis*-lactones from which they were prepared had a rotation of $-5·3°$ in a 100 mm. tube. It has, however, already been pointed out that, in the formation of these lactones from camphoric anhydride, racemisation must have taken

place, and the fact that the *cis*-lactones always have a small rotation simply shows that it has not been quite complete.

When the *cis*-lactones are converted into the bromo-acids and then purified by recrystallisation from light petroleum, the externally compensated modifications being less soluble (as is frequently the case) are easily obtained in a pure state, and the traces of the active modifications remain in the mother liquor.

That the light petroleum mother liquor of these inactive bromo-acids contains active substances was proved by direct experiment, but the solutions were unfortunately too highly coloured to allow of exact measurements being made.

D-Tetrahydro-xylic Acid, $C_8H_{15}\cdot CO_2H$.

D-Bromohexahydro-xylic acid dissolves readily in sodium carbonate solution, and if the solution is heated to boiling for a few seconds and then cooled and acidified, an acid separates either at once in the crystalline form, or else as an oil which rapidly solidifies. The solid mass, after drying on a porous plate, melts at about 80°, and is so soluble in organic solvents that it is difficult to purify it by recrystallisation.

It crystallises, however, in the form of pearly plates from dilute methyl alcohol, but the operation is rather troublesome, since, unless exactly the right conditions of concentration and temperature have been found, the acid always separates as an oil.

D-Tetrahydro-xylic acid melts at 87°, and distils without decomposition; it is almost insoluble in water, but readily volatile in a current of steam. On analysis:

0·1571 gave 0·4020 CO_2 and 0·1298 H_2O. C = 69·8; H = 9·2.
$C_9H_{14}O_2$ requires C = 70·1; H = 9·1 per cent.

When left in contact with fuming hydrobromic acid, this acid is rapidly converted into the D-bromohexahydro-xylic acid from which it had been prepared.

Oxidation of D-Tetrahydro-xylic Acid.—When this unsaturated acid is dissolved in dilute sodium carbonate and mixed with potassium permanganate, the latter is instantaneously reduced, and as it seemed probable that results throwing light on the position of the double linking in this acid (p. 1380) might be obtained by studying this oxidation, the following experiment was carried out.

The pure acid (5 grams) was dissolved in dilute sodium carbonate mixed with a quantity of powdered ice and oxidised, in a porcelain dish fitted with a turbine, with small quantities of permanganate until the colour remained permanent for 3 minutes. Sodium sulphite was then added to destroy the excess of permanganate, the

liquid heated to boiling, and the filtrate and washings of the manganese precipitate evaporated to a small bulk. The concentrated solution, after acidifying with acetic acid, gave no precipitate with calcium sulphate, showing that no oxalic acid had been formed. The whole was then acidified with hydrochloric acid and distilled in steam to remove a very small quantity of a volatile substance which appeared to be present. The residue in the steam distillation flask was saturated with ammonium sulphate, and repeatedly extracted with ether, the ethereal solution was dried over calcium chloride and evaporated, when a pale yellow oil was obtained which, after standing over sulphuric acid in a vacuum desiccator for some days, showed no signs of crystallising. It was analysed with the following result:

0·1571 gave 0·3290 CO_2 and 0·1105 H_2O. C = 57·1; H = 7·8.
$C_9H_{14}O_4$ requires C = 58·0; H = 7·5 per cent.

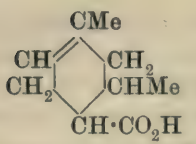
This acid is very readily soluble in water and is monobasic, since 0·207 gram was found, on titration with decinormal caustic soda, to neutralise 0·045 NaOH, whereas this amount of a monobasic acid, $C_9H_{14}O_4$, should have neutralised 0·044 NaOH.

The remainder of the acid was dissolved in water and oxidised with a slight excess of potassium dichromate and dilute sulphuric acid on the water-bath, the product was then saturated with ammonium sulphate and extracted 20 times with ether. After drying over calcium chloride and evaporating, an oil was obtained which on standing over sulphuric acid became semi-solid; when this was spread on a porous plate, the oily impurity was soon completely absorbed, leaving a hard, crystalline mass which melted roughly at 140°.

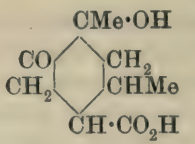
This crude acid is very soluble in water, but a concentrated solution on standing deposits colourless plates like sugar crystals which, after recrystallisation, melt at 167° with slight previous softening. On analysis:

0·1121 gave 0·2206 CO_2 and 0·0704 H_2O. C = 53·6; H = 7·0.
$C_9H_{14}O_5$ requires C = 53·5; H = 6·9 per cent.

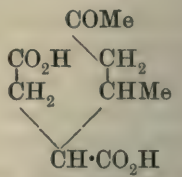
The new acid is dibasic, since 0·1076 gram required for neutralisation 0·0420 NaOH, whereas this quantity of a dibasic acid, $C_9H_{14}O_5$, should neutralise 0·0426 NaOH. It shows all the reactions of a ketonic acid, and when treated with potassium hydroxide and bromine it yields bromoform; it therefore probably contains the group Me·CO; unfortunately, the amount of material at our disposal was too small to allow of the isolation and identification of the acid which is formed during this oxidation. These results seem, nevertheless, to indicate the probability of the oxidation of D-tetrahydro-xylic acid proceeding somewhat in the following way



D-Tetrahydro-xylic acid.



Acid, $C_9H_{14}O_4$.



Acid, $C_9H_{14}O_5$ (m. p. 167°).

The position of the double-bond in D-tetrahydro-xylic acid has, of course, not been definitely ascertained, and the formula given here has simply been selected to serve as an illustration of the possible mechanism of the oxidation.

The Lactone of A-Hydroxyhexahydro-xylic Acid and its Conversion into A-Bromohexahydro-xylic Acid and into A-Tetrahydro-xylic Acid.

Twenty grams of pure A-hydroxyhexahydro-xylic acid (m. p. 160°) were distilled and the distillate dissolved in ether and extracted three times with carbonate of soda to remove traces of an acid which was present (see below). The ethereal solution was then dried over calcium chloride, evaporated and the residual lactone twice fractionated, when practically the whole quantity distilled at 263—265° under 748 mm. pressure the fraction boiling constantly at 264° being collected separately and forwarded to W. H. Perkin, sen., in order that its specific gravity and magnetic rotation might be determined. This specimen had a permanent rotation of +1·96° in a 100 mm. tube. The density and magnetic rotation determinations gave the following results:

Density. d 10°/10° = 1·0640; d 15°/15° = 1·0606; d 20°/20° = 1·0575.

Magnetic rotation.

t.	Sp. rotation.	Mol. rotation.
15·4°	1·0131	8·174.

This *trans*-lactone has therefore a higher sp. gr. and lower magnetic rotation than the *cis*-lactones (p. 1383). During its journey by train, it solidified to a hard mass of crystals which although very soluble in light petroleum (b. p. 30—35°), crystallised from this solvent in colourless needles melting at about 55°. On analysis:

0·1963 gave 0·5034 CO_2 and 0·1641 H_2O. C = 69·9; H = 9·2.
$C_9H_{14}O_2$ requires C = 70·1; H = 9·1 per cent.

In order to prove that this solid lactone was really the *lactone* of *A-hydroxyhydro-xylic acid*, it was warmed with a little baryta water,

in which it very readily dissolved with formation of the barium salt of the hydroxy-acid. The solution was acidified, extracted repeatedly with ether, and the ethereal solution, after drying over calcium chloride, evaporated to a small bulk, when crystalline crusts were deposited which melted at 160° and consisted of pure A-hydroxyhexahydro-xylic acid. The lactone of this acid was previously described (this vol., 345) as an oil boiling at 261—264° under 748 mm. pressure, and this specimen showed no signs of crystallising either after standing for 6 months or on cooling in a mixture of ice and salt; when, however, a crystal of the lactone melting at 55° was put into the liquid, crystallisation started at once and the whole soon solidified to a hard mass of crystals.

The sodium carbonate solution which had been employed in purifying the lactone (see above) gave, on acidifying, no precipitate, but it was noticed that after standing for some days a small quantity of needle-shaped crystals had separated. These were collected and dried on a porous plate at the ordinary temperature; they then melted at 80°, and were found to consist of pure A-tetrahydro-xylic acid (see below). It is therefore evident that A-hydroxyhexahydro-xylic acid on distillation is almost quantitatively converted into its lactone, but that a very small amount of the acid is decomposed in another direction with elimination of water and formation of A-tetrahydro-xylic acid.

A-Bromohexahydro-xylic Acid.—The lactone of A-hydroxyhexahydro-xylic acid dissolves rapidly and completely in fuming hydrobromic acid (saturated at 0°), but the solution soon becomes cloudy and an oily layer separates which becomes crystalline in a few minutes. After standing for about an hour, the hard, crystalline mass was ground up with water, washed well on the pump, dried on a porous plate at the ordinary temperature, and then rapidly recrystallised from boiling light petroleum (b. p. 60—70°). The minute, glistening prisms which rapidly separated were analysed, with the following results:

0·1511 gave 0·1121 AgBr. Br = 33·9.

$C_9H_{15}O_2Br$ requires Br = 34·0 per cent.

A-Bromohexahydro-xylic Acid melts at about 133° almost without decomposition; it is readily soluble in most organic solvents, but only very sparingly so in cold light petroleum; its solution in ether is inactive. In appearance and melting point it is so similar to C-bromohexahydro-xylic acid that we were at first inclined to believe in the identity of the two. We therefore mixed equal quantities of the pure substances, and found that the melting point of the mixture was about 100—105°; it is therefore clear that the acids are not identical.

Considerable quantities of A-bromohexahydro-xylic acid were also prepared by grinding up A-hydroxyhexahydro-xylic acid with fuming

hydrobromic acid. The crystals of the acid become converted into a gummy mass, but this soon solidifies, and after washing well on the pump and drying on a plate, a mass of colourless crystals is obtained which consists of the almost pure A-bromo-acid.

A-Chlorohexahydro-xylic Acid. — When A-hydroxyhexahydro-xylic acid is boiled for a few seconds with concentrated hydrochloric acid, it does not yield the corresponding lactone, but is converted into an oil which, on cooling, solidifies. This was collected, washed well with water, and, after drying over sulphuric acid, rubbed on a porous plate with light petroleum (b. p. 35—40°) until free from traces of oil. The colourless, crystalline residue, which was not sufficient for recrystallisation, melted at about 92°, and, on analysis, gave numbers which showed that it evidently consisted of A-chlorohexahydro-xylic acid:

0·1547 gave 0·1146 AgCl. Cl = 18·3.

$C_9H_{15}O_2Cl$ requires Cl = 18·5 per cent.

A-Tetrahydro-xylic Acid.—This acid is readily obtained by dissolving A-bromohexahydro-xylic acid in excess of sodium carbonate and boiling the solution for a few minutes; it separates on acidifying in an almost pure condition as a colourless, crystalline precipitate. For analysis, it was recrystallised from dilute acetic acid, and thus obtained in the form of colourless groups of needles, which melt at 80°:

0·1587 gave 0·4066 CO_2 and 0·1321 H_2O. C = 69·9; H = 9·2.

$C_9H_{14}O_2$ requires C = 70·1; H = 9·1 per cent.

The acid is almost insoluble in cold water; if, however, it is boiled with water, a small quantity dissolves, and on cooling separates in four-sided plates which melt at 80°; it is readily volatile in steam. Most organic solvents dissolve it freely, but it is comparatively sparingly soluble in cold light petroleum (b. p. 35—40°). The acid seems to have no tendency to yield a lactone on boiling with dilute acids; it separates, for example, unchanged from 20 per cent. sulphuric acid, even after boiling for 5 minutes. When mixed with fuming hydrobromic acid, it becomes soft, but does not dissolve, and from the mixture, after standing for 3 hours, water precipitates a mass of colourless crystals which, after washing with water, drying on a porous plate, and recrystallising from light petroleum, melts at 133°, and consists of pure A-bromohexahydro-xylic acid.

Oxidation of A-Tetrahydro-xylic Acid.—This acid, when dissolved in sodium carbonate, instantly decolorises permanganate, even at temperatures considerably below 0°, and it therefore seemed possible that, by studying this oxidation, results might be obtained which would throw some light on the position of the double bond in the molecule (see p. 1380).

Six grams of the pure acid were therefore dissolved in dilute sodium carbonate, mixed with powdered ice, and treated with a 3 per cent. solution of permanganate until the pink colour remained permanent for at least 2 minutes.

The slight excess was then removed with sodium sulphite, the whole heated to boiling, filtered, and the filtrate and washings of the manganese precipitate evaporated to a small bulk and tested for oxalic acid, but no trace of this acid could be detected. After acidifying and extracting repeatedly with pure ether, the ethereal solution was dried over calcium chloride and evaporated, when a thick, brownish, oily acid was obtained, which was left over sulphuric acid in a vacuum desiccator for 4 days and then analysed, with the following result:

0·1254 gave 0·2622 CO_2 and 0·0887 H_2O. C = 57·0; H = 7·9.
$C_9H_{14}O_4$ requires C = 58·0; H = 7·5 per cent.

This acid is readily soluble in water, and is evidently ketonic in character, since its aqueous solution gives at once a yellow, oily precipitate with phenylhydrazine acetate. That it is monobasic is shown by the results of the titration with decinormal sodium hydroxide, when 0·2366 gram required for neutralisation 0·0508 gram NaOH, whereas this quantity of a monobasic acid, $C_9H_{14}O_4$, should neutralise 0·0509 gram NaOH.

We next oxidised this acid with potassium dichromate and dilute sulphuric acid, exactly as described in the case of the isomeric acid from D-tetrahydro-xylic acid (p. 1389), and on extracting the product with ether, an oily acid was obtained which did not crystallise even after standing over sulphuric acid in a vacuum desiccator for some weeks. This oil gives an oily precipitate with phenylhydrazine acetate, and yields bromoform in considerable quantity when treated with bromine and potassium hydroxide; it is, therefore, evidently a ketonic acid, but as it did not solidify it was not further investigated.

Formation of B-Bromohexahydro-xylic Acid and of B-Tetrahydro-xylic Acid from the Lactone of B-Hydroxyhexahydro-xylic Acid.

The lactone used in these experiments was prepared by distilling the pure B-hydroxy-acid as described in the previous communication, it boiled at 258—260° under 745 mm. pressure and melted at 44°; it was particularly noticed that even after repeated distillation there was no appreciable alteration in the melting point, clearly proving that even at the high temperature of the distillation, no change into a *cis*-modification takes place. When this lactone is melted and mixed with three times its volume of fuming hydrobromic acid (saturated at 0°), it dissolves, but the solution suddenly becomes opaque and an oil

separates which begins to crystallise at once, the change from B-lactone to crystalline bromo-acid being apparently even more rapid than when the A-lactone is similarly treated (p. 1391). The product was mixed with water, the crystals collected, allowed to dry on a porous plate at the ordinary temperature, and then crystallised from light petroleum (b. p. 60—70°). On analysis :

0·1520 gave 0·1212 AgBr. Br = 33·8.
$C_9H_{15}O_2Br$ requires Br = 34·0 per cent.

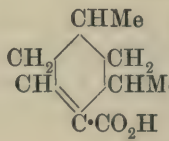
B-Bromohexahydro-xylic Acid melts at about 128° with decomposition, and is more readily soluble in light petroleum than the corresponding A-acid. It dissolves easily in sodium carbonate, and if the solution is boiled for a few minutes, then cooled and acidified, a crystalline precipitate separates which, after crystallising from dilute acetic acid, melts at about 68° and consists of B-tetrahydro-xylic acid.

0·1592 gave 0·4078 CO_2 and 0·1303 H_2O. C = 69·9 ; H = 9·1.
$C_9H_{14}O_2$ requires C = 70·1 ; H = 9·1 per cent.

B-Tetrahydro-xylic Acid is very sparingly soluble in cold water, but it may be crystallised from large quantities of boiling water ; its solution in sodium carbonate instantly decolorises permanganate.

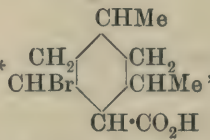
When left in contact with fuming hydrobromic acid, it becomes soft but does not dissolve, and if after 2 hours water is added, a white, crystalline precipitate separates which crystallises from light petroleum in woolly needles melting at 128° and consisting of pure B-bromohexahydro-xylic acid.

Δ^1-*Tetrahydro-xylic Acid,*



and its conversion into

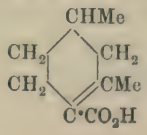
2-*Bromohexahydro-xylic Acid,**



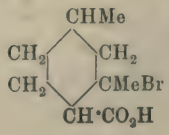
and into Xylic Acid.

Δ^1-Tetrahydro-xylic acid is structurally isomeric with the tetrahydro-xylic acids, A, B, and D, and is the acid which is formed when

* The only other formulæ possible for these acids are :



and



xylic acid is reduced with sodium and *iso*amyl alcohol, and when methyl α-bromohexahydro-xylate is hydrolysed with alcoholic potash (Bentley and Perkin, Trans., 1897, 71, 173; Lees and Perkin, this vol., 338), it melts at 107°. When it is mixed with fuming hydrobromic acid, it does not readily dissolve, but the crystals are seen to undergo gradually a change in appearance. In order to ensure the reaction being complete, the mixture was sealed up in a tube and shaken from time to time, and after two days water was added, the crystals collected on the pump, and allowed to dry on a porous plate in contact with air. The substance then melted at about 124—125°, but after crystallising from light petroleum (b. p. 50—60°), colourless, glistening prisms were obtained which melted at 127° without decomposition. On analysis:

0·152 gave 0·1208 AgBr. Br = 33·8.

$C_9H_{15}O_2Br$ requires Br = 34·0 per cent.

When treated with sodium carbonate, *2-bromohexahydro-xylic acid* shows quite a different behaviour from that observed in the case of the A, B, and D-bromohexahydro-xylic acids (pp. 1388, 1392, 1394). It dissolves at first in the sodium carbonate, forming a clear solution which then rapidly becomes cloudy, and an oil separates which is very readily volatile in steam, smells like a hydrocarbon, and is evidently tetrahydro-*m*-xylene.

$$C_9H_{15}O_2Br = C_8H_{14} + HBr + CO_2.$$

After boiling until the hydrocarbon was expelled, the clear solution gave on acidifying a colourless, crystalline precipitate which, when drained on a tile and dried at 90°, melted sharply at 107—108°, and evidently consisted of Δ^1-tetrahydro-xylic acid.

Action of Sulphuric Acid on Δ^1-*Tetrahydro-xylic Acid.*—This acid dissolves in concentrated sulphuric acid, and when the solution is heated at 100° for 10 minutes, sulphur dioxide is rapidly evolved and the dark coloured liquid, on dilution with water, deposits a yellow, crystalline precipitate. This was collected, distilled, and recrystallised from dilute acetic acid, when colourless crystals were obtained which melted at 124° and consisted of xylic acid. It is therefore evident that, in its behaviour with hydrobromic acid and with sulphuric acid Δ^1-tetrahydro-xylic acid shows the greatest similarity to the A, B, and D tetrahydro-xylic acids described in this paper.

In conclusion we wish to express our thanks to Professors F. S. Kipping and W. J. Pope for many valuable suggestions that they were good enough to make during the course of this research.

We also wish to state that the cost of the large amount of material which was required in this research has been to a large extent defrayed by repeated grants from the Government Grant Fund of the Royal Society.

THE OWENS COLLEGE,
MANCHESTER.

CXLVI.—*Brazilin and Hæmatoxylin. Part I.*

By A. W. GILBODY, W. H. PERKIN, jun., and J. YATES.

BRAZIL-WOOD, or Red-wood, which was originally imported from the East Indies, has been used in Europe for dyeing purposes from very early times and certainly before the discovery of America.

Thus, about the year 1190, the Spanish writer Kimichi mentions dye-woods called Bresil or Brasil (from *braza*, fiery-red), and when the Spaniards discovered South America in 1500, it is probable that they named the northerly portion Brazil, after the dye-wood which is found there in such immense quantities. The Brazil-wood tree belongs to the *Leguminosæ*, species *Cæsalpinia*, and is widely distributed in the Tropics, in the East Indies, South and Central America, the Antilles, and Africa. The most valued Brazil-wood (Fernambukholz, bois de Fernambouc) is obtained from *Cæsalpinia Crista* and *C. brasiliensis*, large crooked trees, with knotty stems, which occur in great numbers in the forests of Brazil and Jamaica.

The wood, which comes into the market in round blocks, is very hard and of a deep red colour; when freshly cut, the colour is light yellow, but this rapidly changes to red in contact with the air. The crude material is rasped and extracted, either by simply boiling with water, or by heating with water under pressure, the liquid is then concentrated in vacuum pans, the actual extract sent into the market varying very much in strength.

Brazil-wood extract is still used in dyeing, but to a comparatively limited extent, owing to the fugitive character of the colours which it yields. It is fixed on the fibre usually in the form of its aluminium or tin lakes, which, although less brilliant and fast than the corresponding alizarine lakes, are somewhat similar to these in appearance.

Brazilin, the actual colouring matter of Brazil-wood, often separates from the commercial extracts in the form of dark brown, crystalline crusts, and pure brazilin is comparatively easily obtained from this crude material by repeated recrystallisation from water containing a small quantity of sulphurous acid, from which solution it separates in pale yellow prisms. The first chemist to isolate brazilin in a crystal-

line form appears to have been Chevreul (*Ann. Chim.*, 1808, [i], **66**, 225), but no attempt was made to determine its constitution until Bolley (*Schweiz. polyt. Zeitsch.*, 1864, **9**, 267) suggested the formula $C_{22}H_{20}O_7$, as the result of several analyses; Kopp (*Ber.*, 1873, **6**, 446) subsequently repeated the analyses and considered the formula $C_{22}H_{18}O_7$ as more probable. It was, however, left to Liebermann and Burg (*Ber.*, 1876, **9**, 1883) to determine accurately the composition of brazilin, and the formula, $C_{16}H_{14}O_5$, which they proposed is that which is used at the present day. The first important step which afforded any evidence of the constitution of brazilin is due to Kopp (*loc. cit.*), who showed that when submitted to dry distillation, this substance yields, besides tar, considerable quantities of resorcinol and, indeed, the yield is so good that this method was for a long time used for its preparation. Before this, Bolley (*loc. cit.*) had treated brazilin with nitric acid and obtained a yellow substance which he imagined to be picric acid, but which Reim (*Ber.*, 1871, **4**, 334) subsequently showed was trinitroresorcinol or styphnic acid, $C_6H(NO_2)_3(OH)_2$.

At a somewhat later date, Liebermann and Burg (*loc. cit.*) showed that resorcinol is also produced in quantity when brazilin is fused with potash, and thus it was early recognised that brazilin is a derivative of resorcinol. The same chemists also proved that brazilin contains four hydroxy-groups, since when treated with acetic anhydride it is converted into a crystalline, colourless, *tetracetyl* derivative, $C_{16}H_{10}O(OAc)_4$. This was subsequently confirmed by Dralle (*Ber.*, 1884, **17**, 375) who, by treating brazilin with sodium methoxide and methyl iodide, obtained *trimethylbrazilin*, $C_{16}H_{10}O(OMe)_3{\cdot}OH$, a substance which still contains a hydroxyl group, since it yields an acetyl compound and when heated in benzene solution with sodium and methyl iodide at 120° is converted into *tetramethylbrazilin*, $C_{16}H_{10}O(OMe)_4$. Of the four hydroxy-groups in brazilin, three are therefore easily methylated, whereas the fourth is not; for this reason it was assumed that whereas the three are aromatic or phenolic, the fourth is alcoholic, and a further examination of the properties of brazilin has shown that this assumption is correct.

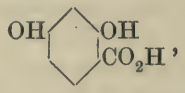
When brazilin is oxidised, it loses two atoms of hydrogen and is converted into *brazilein*,

$$C_{16}H_{14}O_5 + O = C_{16}H_{12}O_5 + H_2O.$$

This change takes place under various conditions; thus Liebermann and Burg (*loc. cit.*) obtained crude brazilein by exposing an alkaline solution of brazilin to the air and by treating an alcoholic solution of brazilin with iodine. Hummel and A. G. Perkin (*Ber.*, 1882, **15**, 2343) prepared pure crystalline brazilein by passing air through a solution of brazilin in ammonia. Buckha and Erck (*Ber.*, 1884, **17**

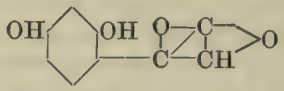
685; 1885, **18**, 1140) obtained brazilein by oxidising brazilin with small quantities of nitric acid, and Schall and Dralle (*Ber.*, 1890, **23**, 1433) by treating its solution in glacial acetic acid with sodium nitrite.

If air is passed through a solution of brazilin in dilute alkali for a considerable time, the purple colour of the solution gradually changes to a reddish-brown and the brazilein which is first produced is completely oxidised. Schall and Dralle (*Ber.*, 1888, **21**, 3017; 1889, **22**, 1559; 1892, **25**, 19), who first studied this oxidation, isolated from the product β-resorcylic acid,

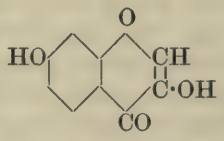


and a substance, $C_9H_6O_4$, which crystallised in needles melting at 271° and contained two hydroxyl groups, since it yielded a *diacetyl* compound, $C_9H_4O_2(OAc)_2$, and a *dimethyl ether*, $C_9H_4O_2(OMe)_2$.

This dimethyl ether, on treatment with acetic acid and permanganate, is oxidised to p-*methoxysalicylic acid*, $C_6H_3(OMe)(OH)\cdot CO_2H$, and on this account and also because the substance $C_9H_6O_4$ does not combine with hydroxylamine or phenylhydrazine, they first assigned to it the constitution

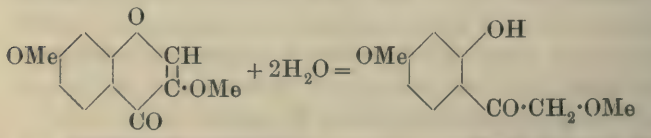


Schall (*Ber.*, 1894, **27**, 528) afterwards suggested that this substance, $C_9H_6O_4$, might possibly be a *phenyl-γ-pyrone* derivative of the formula



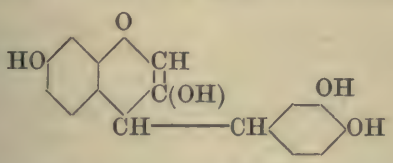
and this view was subsequently proved by Feuerstein and Kostanecki (*Ber.*, 1899, **32**, 1025) to be correct.

These chemists showed that when the dimethyl ether of this substance is boiled with sodium ethoxide it is converted into fisetol dimethyl ether (Herzig, *Monatsh.*, 1891, **12**, 187) with elimination of formic acid, a decomposition which is evidently represented thus:



Dimethyl ether of $C_9H_6O_4$. Fisetol dimethyl ether.

This proof of the constitution of the substance $C_9H_6O_4$, taken in connection with the results which had been obtained by Herzig (*Monatsh.*, 1898, **19**, 738) and by us (see below) led Feuerstein and Kostanecki (*loc. cit.*, p. 1028) to suggest the formula



as probably representing the constitution of brazilin.

Oxidation of Trimethylbrazilin with Potassium Permanganate.

During the course of a long series of experiments on the constitution of brazilin and hæmatoxylin which have been in progress since 1883 and some of the results of which have lately been published as abstracts in the Proceedings (1899, **15**, 27, 75, and 241 ; 1900, **16**, 105 and 107), we have carefully studied the behaviour of trimethylbrazilin, $C_{16}H_{11}O_2(OMe)_3$, with permanganate under very varied conditions. We obtained in this way, besides oxalic, acetic, and formic acids, the following important oxidation products, the investigation of which has thrown much light on the problem of the constitution of brazilin.

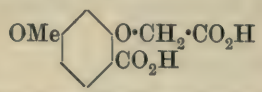
A.	An acid of the formula	$C_{10}H_{18}O_9$,	m. p.	208°.
B.	,, ,,	$C_{10}H_{10}O_6$,	,,	174 .
C.	,, ,,	$C_{10}H_{10}O_6$,	,,	195 .
D.	,, ,,	$C_{12}H_{12}O_6$,	,,	129 .

In the present paper, the description and determination of the constitution of the acids B and C are given in detail, the investigation of the acids A and D, called *brazilinic* and *brazilic* acids respectively, and their decomposition products is not yet complete and will form the subject of a future communication.

Examination of the Acid B of the Formula $C_{10}H_{10}O_6$ *and Melting Point* 174°.—This acid crystallises from water in long needles ; it is dibasic, since it yields a *silver* salt, $C_{10}H_8O_6Ag_2$, it contains one methoxy-group, and when fused with potash is decomposed with formation of a substance which, since it gives with ferric chloride an intense violet coloration, is probably a derivative of resorcinol.

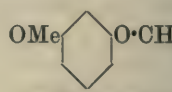
When the aqueous solution of this acid is heated with water at 200°, carbon dioxide is eliminated and a monobasic acid, $C_9H_{10}O_4$ (m. p. 118°), is produced, and this behaviour, taken in conjunction with the fact that brazilin under various conditions yields *p*-methoxy-

salicylic acid, suggested to us that the constitutions of the two acids, $C_{10}H_{10}O_6$ and $C_9H_{10}O_4$, are very probably represented by the formulæ,



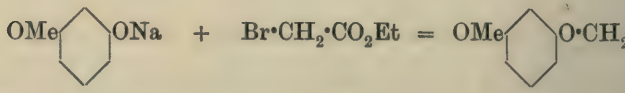
2-Carboxy-5-methoxyphenoxyacetic acid.

and



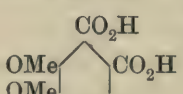
m-Methoxyphenoxyacetic acid.

In order to prove these formulæ, we determined to attempt the synthesis of the acid $C_9H_{10}O_4$ and ultimately succeeded in doing this by treating the sodium compound of resorcinol monomethyl ether with ethyl bromoacetate.

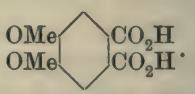


The m-*methoxyphenoxyacetic acid*, which was obtained by hydrolysing the product, melted at 118° and was identical with the acid $C_9H_{10}O_4$ produced by heating the acid $C_{10}H_{10}O_6$. There can therefore be no doubt that the latter is 2-*carboxy*-5-*methoxyphenoxyacetic acid* and has the constitution represented by the formula given above.

Examination of the Acid C of the Formula $C_{10}H_{10}O_6$ *and of Melting Point about* 195°.—This acid crystallised from its dilute aqueous solution in flat prisms containing 2 mols. of water of crystallisation and from concentrated solutions it separated in long, thin needles which were anhydrous. It is a dibasic acid, yielding a *silver* salt, $C_{10}H_8O_6Ag_2$, and an *anhydride* melting at 175°. When heated with hydrochloric acid at 180°, it was completely decomposed into carbon dioxide and catechol, and since it contains two methoxy-groups, its constitution must be represented by one of the formulæ



Hemipinic acid.



m-Hemipinic acid.

Since the melting points, or rather the decomposing points, of these two acids depend so much on the rapidity with which the determination is made and the anhydrides melt at approximately the same temperatures, advantage was taken of the wide difference in the melting points of their ethylimides, $(OMe)_2C_6H_2(CO)_2NEt$, in order to distinguish between them. Goldschmiedt (*Monatsh.*, 1888, **9**, 339) first showed that whereas the ethylimide of hemipinic acid melts at 98°, the corresponding derivative of *m*-hemipinic acid does not melt until 230°. Experiment showed that the ethylimide of the acid from tri-

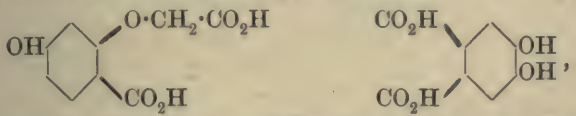
methylbrazilin melted at 230° and therefore there can be no doubt that this acid is m-*hemipinic acid.*

The isolation of *m*-hemipinic acid and of catechol from the products of the oxidation of trimethylbrazilin is a result of great importance, since it proves that brazilin, besides being a resorcinol derivative, also contains a catechol nucleus.

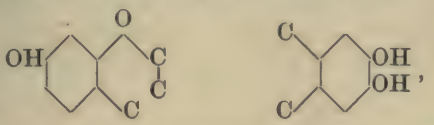
It should be mentioned, however, that shortly before the publication of this result (Proc., 1899, **15**, 27), Herzig (*Monatsh.*, 1898, **19**, 738) had shown that when brazilin is fused with potassium hydroxide it yields a small quantity of an acid which he identified by its melting point and colour reaction with ferric chloride as protocatechuic acid, so that he was actually the first to discover that brazilin is a derivative of catechol.

The Constitution of Brazilin.

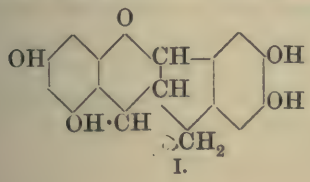
The isolation of 2-carboxy-5-methoxyphenoxyacetic acid and *m*-hemipinic acid from the products of the oxidation of trimethylbrazilin not only proves that brazilin contains both resorcinol and catechol nuclei, but the structure of these acids also affords most valuable evidence as to the way in which these two nuclei are linked together. If the formulæ of the two acids are written side by side without their methyl groups,



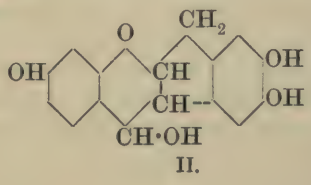
it is clear that in the formula of brazilin these two nuclei must be united in the positions indicated by the dark lines. If now the skeleton formulæ of these two acids be written thus,



it is at once evident that in constructing a constitutional formula for brazilin, $C_{16}H_{14}O_5$, these two residues, which contain C_{17}, must be fused together in such a way that one carbon atom is common to both. Since it is known that in the centre portion, between the two nuclei, brazilin contains an alcoholic hydroxy-group, it seems to us that there can hardly be a doubt that one of the two following formulæ represents the constitution of this substance.

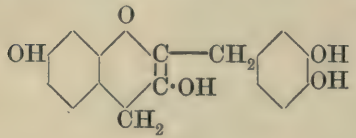


I.

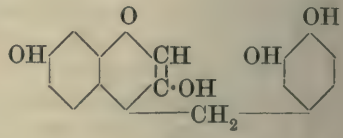


II.

It is obvious that neither formula III, first proposed by Gilbody and Perkin (Proc., 1899, **15**, 75), nor formula IV, suggested by Feuerstein and Kostanecki (*Ber.*, 1899, **32**, 1028),



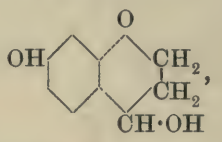
III.



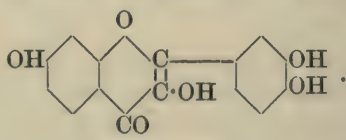
IV.

can possibly represent brazilin, since neither of these gives any explanation of the formation of 2-carboxy-5-methoxyphenoxyacetic acid or of *m*-hemipinic acid by the oxidation of trimethylbrazilin. On the other hand, both formulæ I and II not only account in a satisfactory manner for the formation of these acids, but they are also in agreement with all the other properties of brazilin which are known at the present time.

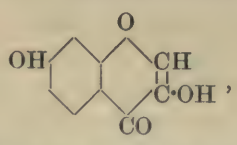
The new formulæ, I and II, represent brazilin as a derivative of a *tetrahydropheno-γ-pyrone* of the formula



a group of atoms that does not appear to have been met with in any of the natural colouring matters hitherto investigated. These formulæ for brazilin are, nevertheless, very similar to those of some of the natural colouring matters and bear considerable resemblance especially to that of fisetin which Herzig (*Monatsh.*, 1894, **15**, 688) and Kostanecki (*Ber.*, 1895, **28**, 2302) have shown to have the constitution

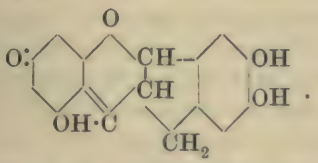


Herzig (*Monatsh.*, 1901, **22**, 209) has lately expressed the opinion that although the formation of 2-carboxy-5-methoxyphenoxyacetic acid and *m*-hemipinic acid from trimethylbrazilin practically proves the position of all the carbon atoms in the molecule, there is still no actual proof of the existence of a γ-pyrone ring in brazilin. Since, however, Feuerstein and Kostanecki (*loc. cit.*) have conclusively proved that the substance $C_9H_6O_4$ obtained by Schall (*loc. cit.*) by passing air through an alkaline brazilin solution is a pheno-γ-pyrone derivative of the formula



it appears to us that there can scarcely be a doubt that brazilin itself also contains a γ-pyrone ring.

As soon as it has been decided which of the formulæ I or II is to be accepted as representing brazilin, $C_{16}H_{14}O_5$, the probable constitution of brazilein, $C_{16}H_{12}O_5$, may be deduced by assuming that the two hydrogen atoms which are removed in the conversion of the former into the latter are derived from the CH·OH group and the hydroxyl group of the resorcinol nucleus. If formula I be taken as an example, the formula of brazilein deduced in this way would be



This relationship between brazilin and brazilein can, however, not be considered proved until it has been found possible to reconvert the latter into the former by reduction.

Preparation of Trimethylbrazilin, $C_{16}H_{11}O_2(OMe)_3$.

The trimethylbrazilin required for this research was prepared by Schall and Dralle's method (*Ber.*, 1888, **21**, 3009), but during the course of the preparation of several kilos. of the substance we found it advantageous to introduce slight modifications into the process, which we now conduct as follows.

Brazilin (143 grams) is dissolved in the smallest possible quantity of hot absolute methyl alcohol, and mixed in a large flask connected with a reflux apparatus, with a solution of sodium (35 grams) in methyl alcohol, an operation which causes the separation of a mass of crystals, consisting probably of the trisodium compound of brazilin. A slight excess of methyl iodide (250 grams) is then added and after well mixing, the flask is immersed in a large water-bath and heated at 60—65° day and night for 50 hours, the temperature being kept constant by a regulator and access of air avoided as far as possible by inserting a stopper of cotton wool into the open end of the condenser. The product is poured into about 6 litres of water, allowed to stand for 24 hours, and the precipitate, after collecting on the pump and washing with water, is transferred to large flasks and extracted with warm ether until all the trimethylbrazilin has been dissolved. The ethereal

extract is shaken repeatedly with sodium hydroxide, dried over calcium chloride and evaporated to a small bulk, when on standing and even during the concentration, the trimethylbrazilin separates as a pale yellow, crystalline mass, which after washing on the pump with ether is almost pure and in this condition was used in all our experiments.

During the extraction of the crude trimethylbrazilin with ether, the impurities first dissolve, the mass becomes more and more sparingly soluble, and ultimately a peculiar, brownish-violet residue is obtained, which closely resembles amorphous phosphorus in appearance and is apparently quite insoluble in ether.

Although somewhat tedious, the purification with ether is much to be preferred, as the alternative method, namely, crystallisation from alcohol, is more wasteful and frequently does not give at once so pure a product. The yields we obtained usually from 1 kilo. of brazilin were 950 grams of crude product, which on extraction with ether yielded about 700 grams of trimethylbrazilin and 60 grams of the brownish-violet, insoluble residue, the remainder consists largely of dimethylbrazilin which is dissolved out during the treatment of the ether extract with sodium hydroxide, and partly of uncrystallisable resins remaining in the ethereal mother liquors of the trimethylbrazilin.

A specimen of trimethylbrazilin which had been purified by recrystallisation from ether was analysed with the following results:

0·1612 gave 0·4102 CO_2 and 0·0888 H_2O. C = 69·4; H = 6·1.
$C_{16}H_{11}O_2(OMe)_3$ requires C = 69·5; H = 6·1 per cent.

A methoxyl determination by Zeisel's method gave the following result:—

0·2121 gave 0·4631 AgI. OCH_3 = 29·1.
$C_{16}H_{11}O_2(OMe)_3$ requires OH_3 = 28·2 per cent.

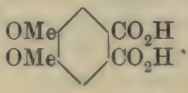
Oxidation of Trimethylbrazilin with Potassium Permanganate.

When ground up into a fine paste with water, trimethylbrazilin is slowly attacked at the ordinary temperature by permanganate and in our earlier experiments much material was oxidised in this way. A long series of comparative trials showed, however, that there was not much difference in the yield of acids produced at 15° and at 90°, and as oxidation is much more rapid at 90°, we have during the last two years worked almost entirely at this temperature. The oxidation is now carried out as follows. Trimethylbrazilin (10 grams) is ground up into an exceedingly fine paste with a little water, washed into a 4-litre flask with about 500 c.c. of hot water, and a cold saturated solution of potassium permanganate added in small quantities at a time, with repeated shaking, the flask being heated during the whole operation on

the water-bath. As soon as the colour of the permanganate remains permanent for several minutes (which is the case after about 1½ hours), the excess is destroyed by the addition of a little sodium sulphite, and the whole filtered on the pump by means of a Buchner funnel.

The manganese precipitate is ground up with hot water and filtered again, and, after repeating this operation, the washings are added to the original filtrate, the whole nearly neutralised with hydrochloric acid and evaporated to a small bulk, first in an enamelled basin over the free flame and then on the water-bath.

During this operation, a small quantity of a crystalline precipitate is usually deposited; this was collected and found to consist of unchanged trimethylbrazilin. On acidifying the cold, slightly brownish-coloured liquid with hydrochloric acid, it becomes pink and deposits a red, resinous precipitate. This is extracted repeatedly with small quantities of chloroform. The chloroform solution is then dried over calcium chloride and evaporated, and the reddish-brown, resinous residue, which contains *brazilinic acid* and *brazilic acid*, treated as described on p. 1410. The aqueous solution, which had been extracted with chloroform, is saturated with ammonium sulphate and extracted at least 20 times with ether. The ethereal solution is then dried over calcium chloride and evaporated to a small bulk, when, on standing, it deposits a yellow, crystalline precipitate, which consists almost entirely of m-*hemipinic* acid and 2-*carboxy*-5-*methoxyphenoxyacetic acid.*

m-*Hemipinic Acid*, 

The crude mixture of *m*-hemipinic acid and 2-carboxy-5-methoxyphenoxyacetic acid, obtained as just described, was recrystallised once from water with the aid of animal charcoal and then distilled under 55 mm. pressure, when almost the whole quantity passed over at 172° as a yellow oil, which, on cooling, solidified and consisted of a mixture of *m*-hemipinic anhydride and 2-carboxy-5-methoxyphenoxyacetic acid. It was dissolved in the smallest possible quantity of boiling toluene and the crystals which separated on cooling and those obtained by concentrating the toluene filtrate, were finely powdered and extracted repeatedly with small quantities of dilute sodium carbonate. The insoluble m-*hemipinic anhydride* was then crystallised from toluene, from which it separated in pale yellow crystals melting at 175°. On analysis:

0·1661 gave 0·3521 CO_2 and 0·0607 H_2O. C = 57·8; H = 4·0.

$C_{10}H_8O_5$ requires C = 57·7; H = 3·8 per cent.

This anhydride dissolves readily in dilute methyl alcoholic potash,

and if the solution is evaporated until free from the alcohol and then acidified, a woolly mass of needles separates, which, after washing with a little water on the pump, consists of pure m-*hemipinic acid*. On analysis:

0·1168 gave 0·2272 CO_2 and 0·0481 H_2O. C = 53·0; H = 4·5.
$C_{10}H_{10}O_6$ requires C = 53·1; H = 4·4 per cent.

A methoxyl determination by Zeisel's method furnished the following result:

0·3457 gave 0·6890 AgI. OCH_3 = 26·3.
$(OCH_3)_2C_6H_2(CO_2H)_2$ requires OCH_3 = 27·4 per cent.

The pure *m*-hemipinic acid obtained in this way, when moderately rapidly heated, softens at 190° and decomposes quite sharply at 194—195° into water and the anhydride, but other specimens prepared during this research, which had not been purified by conversion into the anhydride, showed a lower and much less sharp melting or decomposing point; according to Goldschmiedt (*Monatsh.*, 1885, **6**, 380), *m*-hemipinic acid melts when rapidly heated at 179—182°, and as there is thus a slight discrepancy in the melting points, it became necessary to sharply characterise the acid from brazilin.

In the first place, it was repeatedly noticed that the latter acid has the property of crystallising in two entirely different ways, thus, when it separates rapidly from a strong solution in hot water, it is obtained in needles which are anhydrous, but if its saturated aqueous solution is allowed to evaporate at the ordinary temperature, glistening prisms are deposited which contain 2 mols. of water of crystallisation, as the following determination shows:

0·4371, at 100°, lost 0·0596 H_2O H_2O = 13·8.
$C_{10}H_{10}O_6,2H_2O$ requires H_2O = 13·7 per cent.

This capability of crystallising in two such distinct forms is one of the characteristics of *m*-hemipinic acid.

m-*Hemipinethylimide*, $(OMe)_2C_6H_2(CO)_2NEt$.—In order to be quite certain that the acid was *m*-hemipinic acid, a small quantity was dissolved in water, made strongly alkaline with ethylamine, evaporated to dryness, and the residue distilled from a small retort. The yellow, crystalline distillate separated from alcohol, in which it is very sparingly soluble, in yellow needles melting at 230° and consisted of pure *m*-hemipinethylimide. On analysis:

0·2241 gave 11·9 c.c. nitrogen at 19° and 757 mm. N = 6·1.
$C_{12}H_{13}O_4N$ requires N = 5·9 per cent.

Goldschmiedt gives 230° as the melting point of the ethylimide of the *m*-hemipinic acid which he obtained from papaverine.

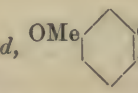
Formation of Catechol from m-Hemipinic Acid by the Action of Hydrochloric Acid.—This experiment was carried out before it was known that the acid obtained from trimethylbrazilin was *m*-hemipinic acid. The pure acid (2 grams) was heated in a sealed tube with concentrated hydrochloric acid at 185° for an hour, when on opening the tube there was considerable pressure, and the gas which escaped burnt with a green edged flame and was doubtless methyl chloride. This gas also contained carbon dioxide, as was shown by leading it through baryta water. The contents of the tube were filtered from a few black specks, the filtrate extracted 10 times with ether, and the ether evaporated, when an oily residue was obtained, which on standing over sulphuric acid crystallised in large plates. The crystals were left in contact with a porous tile until quite dry and recrystallised from benzene with the aid of animal charcoal; the colourless prisms thus obtained were analysed:

0·1671 gave 0·4012 CO_2 and 0·0830 H_2O. C = 65·5; H = 5·5.
$C_6H_6O_2$ requires C = 65·5; H = 5·5 per cent.

This substance melted at 104—105° and its solution in water gave with ferric chloride an intense green coloration, which on the addition of ammonium carbonate became first violet and then red. There can be no doubt that it is catechol, since a small quantity mixed intimately with an equal weight of a pure sample of catechol melted at 104°. It is therefore clear that *m*-hemipinic acid, when heated with hydrochloric acid at 185°, is decomposed according to the equation

$$(OMe)_2C_6H_2(CO_2H)_2 + 2HCl = C_6H_4(OH)_2 + 2CO_2 + 2MeCl.$$

This decomposition had not previously been observed, and it is certainly remarkable that the two carboxyl groups attached to the benzene nucleus should be so easily and completely removed at this comparatively low temperature. When hemipinic acid is heated with hydrochloric acid at 170°, it behaves differently, protocatechuic acid being produced by the elimination of only one carboxyl group.

2-Carboxy-5-methoxyphenoxyacetic Acid,  .

The sodium carbonate solution, which had been separated from the *m*-hemipinic anhydride as described on p. 1405, gave, on acidifying, a crystalline precipitate, which was collected and purified by recrystallisation from water, from which it separated in long needles. On analysis:

0·1469 gave 0·2863 CO_2 and 0·0603 H_2O. C = 53·1 ; H = 4·5.
0·1912 ,, 0·3736 CO_2 ,, 0·0777 H_2O. C = 53·1 ; H = 4·4.
$C_{10}H_{10}O_6$ requires C = 53·1 ; H = 4·4 per cent.

2-*Carboxy-5-methoxyphenoxyacetic acid* melts at about 174° and seems to have no tendency to form an anhydride, as is shown by the fact that even on distillation it passes over unchanged. It is very sparingly soluble in cold water, but dissolves readily on boiling; it is also sparingly soluble in ether, benzene, or light petroleum, but readily so in methyl alcohol, acetone, or warm acetic acid; from the last of these solvents, it separates on cooling in beautiful, colourless needles. When fused with potassium hydroxide, a product is obtained which, on acidifying and extracting with ether, yields a substance which gives the resorcinol reaction with ferric chloride, and this experiment was the first which afforded us any clue to the constitution of the acid. A determination of the methoxyl group by Zeisel's method was made, with the following result:

0·3784 gave 0·4133 AgI. OCH_3 = 14·40.
$CH_3{\cdot}O{\cdot}C_6H_3(O{\cdot}CH_2{\cdot}CO_2H){\cdot}CO_2H$ requires OCH_3 = 13·72 per cent.

That this acid is dibasic was shown by titration with decinormal sodium hydroxide, when 0·2005 gram of the pure acid required for neutralisation 0·0708 gram NaOH, whereas this amount of an acid, $C_{10}H_{10}O_6$, if dibasic, should neutralise 0·0709 gram NaOH.

The salts of 2-carboxy-5-methoxyphenoxyacetic acid are sufficiently characteristic to be described in some detail.

The *silver* salt, $C_{10}H_8O_6Ag_2$, is obtained as a white, gelatinous precipitate on adding silver nitrate to a slightly alkaline solution of the ammonium salt. On analysis:

0·2565 gave 0·2538 CO_2, 0·0455 H_2O, and 0·1252 Ag. C = 27·0 ; H = 1·9 ; Ag = 48·8.
$C_{10}H_8O_6Ag_2$ requires C = 27·3 ; H = 1·8 ; Ag = 49·1 per cent.

A slightly alkaline solution of the ammonium salt showed the following characteristic behaviour with reagents:

Calcium Chloride gives, in a moderately concentrated solution, a white, amorphous precipitate, which dissolves in warm water, but on boiling separates out again as a very sparingly soluble, amorphous substance. In weaker solutions, calcium chloride gives no precipitate in the cold, but the amorphous calcium salt separates on boiling.

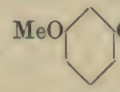
Barium Chloride gives a white, amorphous precipitate which, on warming with water, dissolves, but when the solution is boiled, a very sparingly soluble salt separates in microscopic groups of needles.

Copper Sulphate gives no immediate precipitate in the cold, but, on

standing, an insoluble copper salt slowly separates in pale blue needles; the separation takes place at once on boiling the solution.

Zinc Sulphate.—When this reagent is added to a moderately strong solution of the ammonium salt, the solution remains clear for a few seconds and then suddenly becomes cloudy, owing to the separation of an amorphous zinc salt. If a weak solution is mixed with zinc sulphate and allowed to stand, the zinc salt separates slowly in groups of spherical individuals, which, seen under the microscope, closely resemble yeast cells.

Magnesium Chloride gives no precipitate in the cold, but on boiling, a sparingly soluble salt gradually separates in four-sided plates.

m-*Methoxyphenoxyacetic Acid*,  .

When 2-carboxy-5-methoxyphenoxyacetic acid is heated in a sealed tube with water at 200—210° for 2 hours, decomposition takes place and on opening the tube carbon dioxide escapes. The solution, which is nearly colourless, but contains carbonaceous specks in suspension, is filtered, concentrated, and allowed to stand, when crystals gradually separate, which are purified by recrystallisation from water. On analysis:

0·1192 gave 0·2589 CO_2 and 0·0584 H_2O. C = 59·2; H = 5·4.
0·187 „ 0·4059 CO_2 „ 0·0917 H_2O. C = 59·2; H = 5·5.
$C_9H_{10}O_4$ requires C = 59·3; H = 5·5 per cent.

m-*Methoxyphenoxyacetic acid* softens at 115° and melts at 118°; it is only sparingly soluble in cold, but dissolves readily in hot, water. It has a great tendency to separate from its hot aqueous solution, on cooling, in oily drops, which take some time to solidify, but this may be avoided by keeping the solution moderately dilute and stirring continually with a glass rod on the sides of the beaker during cooling; it is then obtained in the form of slender needles.

Synthesis of m-*Methoxyphenoxyacetic Acid.*—In carrying out this synthesis, 25 grams of resorcinol monomethyl ether, $OMe{\cdot}C_6H_4{\cdot}OH$, which had been carefully freed from all traces of resorcinol by repeated fractional distillation, were dissolved in alcoholic sodium ethoxide (containing 5 grams of sodium), and the solution mixed with 35 grams of ethylic bromoacetate. On heating this mixture in a reflux apparatus on the water-bath, decomposition set in at once, and, after heating for 2 hours, water was added, the whole extracted with ether, and the ethereal solution well washed until free from alcohol, dried over calcium chloride, and evaporated. The oily residue, after twice fractionating under reduced pressure, boiled constantly at 170° (24 mm.), and gave,

on analysis, numbers which show that it consisted of pure *ethyl* m-*methoxyphenoxyacetate*, $OMe{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2Et$.

0·1545 gave 0·3545 CO_2 and 0·0946 H_2O. C = 62·6; H = 6·8.
$C_{11}H_{14}O_4$ requires C = 62·8; H = 6·7 per cent.

Hydrolysis.—When this ester (21 grams) was mixed with a filtered solution of 10 grams of potassium hydroxide in methyl alcohol, a good deal of heat was developed, and in a short time the mass became semi-solid, owing to the separation of a white, crystalline potassium salt. This was collected on the pump, washed well with methyl alcohol, and recrystallised from this solvent; it was thus obtained in colourless needles, which are very sparingly soluble in cold methyl alcohol, but readily soluble in water. The aqueous solution of this salt gave, on acidifying, an oily precipitate which rapidly solidified, and by carefully crystallising from water, colourless needles were obtained, which were analysed, with the following results:

0·1840 gave 0·3998 CO_2 and 0·0932 H_2O. C = 59·3; H = 5·6.
$C_9H_{10}O_4$ requires C = 59·3; H = 5·5 per cent.

The m-*methoxyphenoxyacetic acid* thus obtained softened at 116° and melted at 118—119°; it is identical with the acid obtained from the 2-carboxy-5-methoxyphenoxyacetic acid from brazilin (see above), since an intimate mixture of the two preparations melted at the same temperature as the constituents.

Brazilinic Acid, $C_{19}H_{18}O_9$, *and Brazilic Acid*, $C_{12}H_{12}O_6$.

When the chloroform extract of the acidified oxidation product of trimethylbrazilin (see p. 1405) is left for some days, it usually solidifies, but it was found impossible to obtain any crystalline products directly from it by treatment with organic solvents on account of the considerable quantity of resinous matter which it contains; it may, however, be purified in the following way.

The resinous mass obtained from each 10 grams of trimethylbrazilin is boiled with half a litre of water, filtered from a varying quantity of insoluble tarry matter, the filtrate evaporated to about 100 c.c., and allowed to stand for 2 or 3 days. The crystals which have then separated are collected on the pump, washed with water, and dissolved in a little glacial acetic acid, from which solution the *brazilinic acid* slowly separates in hard, colourless crystals. After recrystallisation, this acid melts at 208° and gives numbers on analysis agreeing with those required for the formula $C_{19}H_{18}O_9$. It therefore contains the same number of carbon atoms as trimethylbrazilin.

0·1722 gave 0·3698 CO_2 and 0·0715 H_2O. C = 58·6 ; H = 4·6.
0·1928 „ 0·4112 CO_2 „ 0·0789 H_2O. C = 58·2 ; H = 4·6.
$C_{19}H_{18}O_9$ requires C = 58·5 ; H = 4·6 per cent.

The aqueous filtrate from the crude brazilinic acid is made slightly alkaline with sodium carbonate and evaporated to a small bulk, when, on standing, crystals of the sparingly soluble sodium salt of brazilic acid gradually separate. This salt is collected on the pump and recrystallised twice from water, from which it separates in satiny plates. It is then dissolved in water and acidified and the voluminous, needle-shaped crystals of the free acid are collected on the pump and purified by crystallisation from water. *Brazilic acid* melts at 129° and is readily soluble in hot, but only sparingly so in cold, water. On analysis :

0·1337 gave 0·2788 CO_2 and 0·0640 H_2O. C = 56·9 ; H = 5·3.
0·1431 „ 0·3003 CO_2 „ 0·0623 H_2O. C = 57·2 ; H = 4·8.
$C_{12}H_{12}O_6$ requires C = 57·2 ; H = 4·8 per cent.

The amount of brazilinic acid obtained by the oxidation of trimethylbrazilin is considerable, 1 kilo. yielding about 50 grams of the pure acid. On the other hand, brazilic acid is only produced in very small quantities, the average yield being about 7 grams from this quantity of trimethylbrazilin. Both these acids are, at the present time, being subjected to a careful examination, and it is hoped that the results which are being obtained will throw much further light on the question of the constitution of brazilin.

We wish at this stage to express our thanks to the Government Grant Committee of the Royal Society for the repeated grants which they have given us in aid of this work.

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ERRATA.

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988	2	*for* "$C_{17}H_{20}O_2$" *read* "$C_{15}H_{16}O_2$."

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1232	16*	,, "1·390" and "39·04" *read* "1·2635" and "35·48."

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1345	22*	i	*for* "T., 237" *read* "T., 327."

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v	4	*for* "Amidosulphate" *read* "Amidosulphite."

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191	8	,, "of" *read* "in."
195	1* & 2*	*delete* "and pressure."
225	12*	*for* "formed by the water" *read* "formed and absorbed by the water"
227	16	,, "1·2127" *read* "0·12127."
230	17	,, "$\frac{\partial x}{\partial y}dy+\frac{\partial y}{\partial x}dx$" *read* "$\frac{\partial \lambda}{\partial y}dy+\frac{\partial \lambda}{\partial x}dx$."
282	23	,, "methyl" *read* "ethyl."
392	19	,, "*Sodamierde Divatives*" read "*Sodamide Derivatives*."
584	16*	,, "2·5 grams" *read* "21 grams."
872	14	*delete* "Robert McClumpha."
1021	3*	*for* "1 : 2-*Dibenzoyl*-1 : 2-*diphenyl*cyclo*pentane*" read "1 : 2-*Diphenyl*-1 : 2-*dihydroxy*cyclo*pentane*."
1022	8	
1028	17*	,, "$C_{24}H_{24}O_2$" *read* "$C_{34}H_{24}O_2$."
1034	4*	,, "Ten" *read* "Forty."
1036	4*	,, "precipitation" *read* "preparation."
1141	8	,, "per cent." *read* "for this amount."

* From bottom.

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